This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

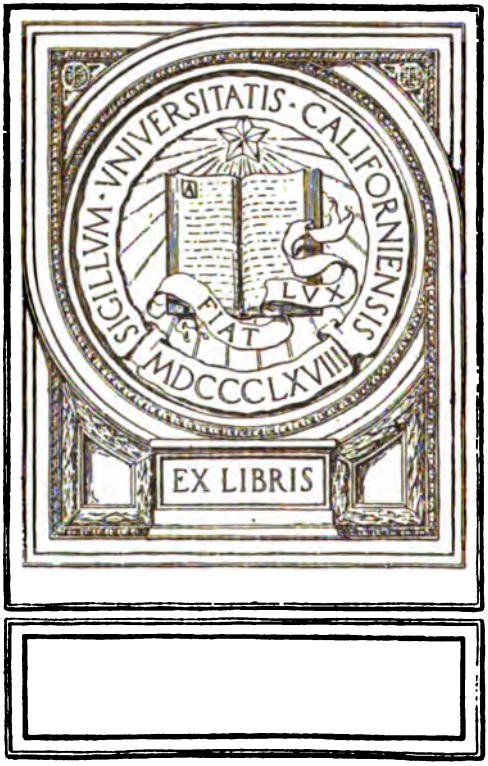
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`



Digitized by Google

Digitized by Google

Digitized by Google

SOME PHYSICO-CHEMICAL THEMES

Digitized by Google

BY THE SAME AUTHOR.

RECENT ADVANCES IN ORGANIC CHEMISTRY. With an Introduction by J. NORMAN COLLIE, LL.D., F.R.S. 8vo, 21s. net.

RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY. With an Introduction by Sir WILLIAM RAMSAY, K.C.B., F.R.S. With 25 Illustrations, and a Curve of Atomic Volumes. 8vo, 18s. net.

CHEMISTRY AND ITS BORDERLAND. Crown 8vo, 6s. 6d. net.

STEREOCHEMISTRY. With 58 Illustrations. 12s. 6d. net. *(Text-Books of Physical Chemistry.)*

LONGMANS, GREEN AND CO.,
London, New York, Bombay, Calcutta, and Madras.

Digitized by Google

SOME PHYSICO-CHEMICAL THEMES

UNIV. OF CALIFORNIA

BY

ALFRED W. STEWART, D.Sc.

PROFESSOR OF CHEMISTRY IN THE QUEEN'S UNIVERSITY OF BELFAST

WITH FIVE PLATES AND THIRTY-SEVEN DIAGRAMS IN THE TEXT

LONGMANS, GREEN AND CO.

39 PATERNOSTER ROW, LONDON, E.C. 4

55 FIFTH AVENUE, NEW YORK

BOMBAY, CALCUTTA, AND MADRAS

1922

Digitized by Google

QD453
S83

Digitized by Google

QD453
S83

PREFACE.

THE student beginning the study of physical chemistry finds himself so well catered for that he has only the difficulty of making his choice among the numerous excellent text-books which have been written for him; but when this stage of his studies is ended and he has acquired a general grasp of the outlines of the subject, he is rather apt to feel himself at a loss if he desires to make further progress. Chemical journals are certainly open to him; but in most cases he has not yet acquired that sense of perspective without which the perusal of Proceedings and Transactions is a somewhat toilsome task; and, in the case of the average student, he hardly knows where to begin. There is at present a lack of works which would bridge the gap between the text-book and the original literature. Monographs on many isolated subjects exist, it is true, but a library of monographs is beyond the means of the average student at the present day, and besides, the reading of a dozen monographs requires more leisure than most hard-pressed students have at their disposal.

It is in view of this situation that the present book has been written. The object which I have kept before me is to provide the reader with brief accounts of a fair number of subjects, some of which have not hitherto been dealt with in books, and to stimulate him, if possible, to seek further information in the original literature. For this reason, no attempt has been made to include the work published in last month's journals. My effort has been to lay a foundation sufficient to allow the student to build up a knowledge of the more recent researches by means of his own reading.

691557

Digitized by Google

I have endeavoured, whenever possible, to keep clearly separate from each other the experimental facts and the hypotheses by means of which attempts have been made to account for these facts, so that the student should be under no illusions as to where facts end and theories begin.

It may also be well to point out that the treatment of the various subjects is not intended to approach the exhaustive. Limitations of space alone would forbid such an attempt. When any subject could not be dealt with at length, I have endeavoured to select those portions which seemed to me most likely to interest a student or to suggest ideas to him; and I believe that such a mode of treatment will fulfil the object I had in view much better than a highly condensed and semi-unreadable description of the whole field would have done. Three of the chapters have appeared in a modified form elsewhere, but as they are now unprocurable they have been introduced into their natural position in this book.

As to the choice of subjects in the volume, it has been guided partly by my own interest and partly by the interest shown in these branches by students. It may be frankly admitted that many other possible selections might have been made; and in some cases a critical reader may lament the omission of topics in which he himself is keenly interested. If this should prove to be the case, I trust that he will take the obvious step to repair the error—by writing a book on these subjects himself.

No attempt has been made to deal with the problems of radioactivity or stereochemistry in the present volume, except incidentally in connection with other subjects.

Since the main object of this book is to be stimulative if possible, I have not hesitated to diverge from the beaten track of the subject and to introduce, here and there, excursions into cognate fields, even when this leads to a certain halt in the main current of the argument.

An examination of the contents of the volume will show that an attempt has been made to avoid a prejudice which makes many books on physical chemistry rather one-sided. Physico-chemical methods are applicable to both organic and inorganic substances; but in some quarters there is an illogical

Digitized by Google

tendency to restrict physical chemistry to a consideration of inorganic compounds. This crotchet produces an undesirable warping of perspective, since it tends to discourage the investigation of one of the most fruitful branches of physical chemistry—the relations between chemical constitution and physical properties. It cannot be too strongly emphasised that a properly trained physical chemist must be conversant with organic as well as inorganic chemistry. He need not be a specialist in the organic branch, but he should at least have sufficient acquaintance with the subject to appreciate the peculiar differences between organic and inorganic reagents.

As the book is intended to help the student to find his way about the literature of the subjects described in it, liberal references to the journals have been given and a short Bibliography has been appended to the volume. Neither of these aids is by any means exhaustive. The abbreviations of the titles of the journals are in the main those employed by the Chemical Society. In order to avoid giving unnecessary trouble to the reader, footnotes are distinguished by asterisks, etc., whilst references to journals are indicated by numbers.

I wish to express my thanks to Dr. R. Wright, Mr. H. Graham, M.Sc., and Mr. F. Stoyle, B.Sc., for assistance and criticism.

I have to thank the Chemical Society for permission to reproduce the diagram illustrating the *Periodic Relations of the Elements* by the late Prof. J. Emerson Reynolds, F.R.S., which appeared in the Journal of that Society.

A. W. STEWART.

THE SIR DONALD CURRIE LABORATORIES,
THE QUEEN'S UNIVERSITY OF BELFAST,
2nd January, 1922.

Digitized by Google

Digitized by Google

CONTENTS.

PAGE

PREFACE v

CHAPTER

I. INTRODUCTION 1

II. RESIDUAL AFFINITY AND SOME PHYSICAL PROPERTIES . . . 7

1. The Meaning of Residual Affinity, 7. 2. Thiele's Theory of Partial Valencies, 9. 3. Space-Conjugation, 14. 4. Boiling-point Relations, 15. 5. Refractivity, 17. 6. Magnetic Susceptibility, 20. 7. Magnetic Rotatory Power, 21. 8. Optical Rotatory Power, 25. 9. Fluorescence and Luminescence, 27. 10. Absorption Spectra, 31. 11. Conclusion, 38.

III. DOUBLE SALTS 39

1. Introductory, 39. 2. Some Chemical Factors Influencing Double Salt Formation, 42. 3. Transition Temperatures, 43. 4. Transition Intervals, 50. 5. The Existence of Double Salts in Solution, 55. 6. Criteria of the Nature of Equimolecular Mixtures of Optical Antipodes, 56.

IV. THE PROBLEM OF THE OCEANIC SALT DEPOSITS 60

1. The Stassfurt Salts, 60. 2. The Researches of Usiglio and van't Hoff, 61. 3. Solutions of Potassium and Sodium Chlorides, 63. 4. The Case of Carnallite, 65. 5. The Case of the Chlorides and Sulphates of Magnesium and Potassium, 68. 6. The Case of Five Salts, 78. 7. The Influence of Time, 75. 8. Paragenesis and the Influence of Temperature, 77.

V. COMPLEX SALTS AND COMPLEX IONS 83

1. Introductory, 83. 2. Proofs of the Existence of Complex Ions in Solution, 84. 3. The Cobaltammines, 91.

VI. THE PSEUDO-ACIDS 96

1. Introductory, 96. 2. Hantzsch's Criteria, 101. 3. The Phenomena of Slow Neutralisation, 103. 4. Abnormal Hydrolysis, 104. 5. Colour Change in Passing from Pseudo-acid to Salt, 105. 6. Abnormal Temperature Coefficients, 107. 7. The Ammonia Reaction, 109. 8. Abnormal Hydrates, 109. 9. Conductivity in Aqueous-alcoholic Solutions, 109. 10. The Refractometric Method, 110. 11. Conclusion, 111.

Digitized by Google

CHAPTER PAGE

VII. The Theory of Indicators 113
1. Ostwald's Ionic Hypothesis, 113. 2. The Intramolecular Change Theory, 115. 3. The Mechanism of Indication, 123. 4. Conclusion, 126.

VIII. Non-Aqueous Ionising Media 128
A. *Introductory* 128
B. *Reactions in Liquid Ammonia* 129
1. The Properties of Liquid Ammonia, 129. 2. Reactions between Inorganic Salts, Bases and Acids in Liquid Ammonia Solutions, 130. 3. The Reactions of Ammonosalts, Ammono-bases and Ammono-acids in Liquid Ammonia Solution, 132.
C. *Walden's Investigations* 134
1. General, 134. 2. Conductivity, Dissociating Power and Dielectric Constant, 135. 3. Conductivity and Viscosity, 140. 4. Solvent Power and Heat of Solution, 142. 5. Refractivity and Molecular Solution Volume, 145. 6. Electrostriction, 148. 7. Solvent Power and Dielectric Constant, 150.
D. *Some Other Relationships* 153
1. Abnormal Cases, 153. 2. Mixed Solvents, 155.

IX. Colloids 158
1. General, 158. 2. The Preparation of Colloidal Solutions, 161. 3. The Osmotic Pressure and Optical Properties of Colloidal Solutions, 164. 4. The Electrical Properties of Colloidal Solutions, 167. 5. The Catalytic Action of Sols, 174. 6. Coagulation, 174. 7. The Properties of Gels, 182.

X. The Brownian Movement 186
1. The Nature of the Brownian Movement, 186. 2. Measurements of the Brownian Movement, 188. 3. The Kinetic Theory and the Brownian Movement, 190. 4. The Brownian Movement in Gases, 193.

XI. Perrin's Researches on the Distribution of Particles in Emulsions 195
1. Introductory, 195. 2. The Preparation of Emulsions, 198. 3. The Theoretical Distribution of Gas Molecules in a Vertical Column, 201. 4. The Observation of Emulsions, 204. 5. Comparison between Theory and Practice in Emulsions, 206. 6. Conclusion, 207.

XII. Avogadro's Constant and some Molecular Dimensions . . 209
1. The Factor N, 209. 2. The Upper Limit of Molecular Diameter, 210. 3. Methods Based on the Kinetic Theory of Gases, 211. 4. The Determination of N from Properties of Emulsions, 216. 5. The Determination of N from Radiation Phenomena, 219. 6. The Determination of N from

Digitized by Google

CHAPTER PAGE

Charges on Gaseous Ions, 222. 7. Methods Depending upon Radioactive Properties, 224. 8. The Distances of Atoms in Crystals, 226. 9. Conclusion, 228.

XIII. Adsorption 231
1. Sorption, Absorption and Adsorption, 231. 2. The Surface Factor, 232. 3. The Phenomena of Adsorption, 237. 4. Adsorption and Chemical Reaction, 243.

XIV. Some Hypotheses of the Colloid State 246
1. Introductory, 246. 2. The Crystalloid Hypothesis, 247. 3. The Solution Hypothesis, 249. 4. The Partition Hypothesis, 249. 5. The Negative Surface Tension Hypothesis, 251. 6. Electrical Hypotheses, 252. 7. Conclusion, 253.

XV. Catalysis 254
1. Some Criteria of Catalytic Action, 254. 2. Positive and Negative Catalysis, 257. 3. Selective Catalysis, 260. 4. The Solvent Medium as a Catalyst, 263. 5. Some Theories of Catalytic Action, 264. 6. Conclusion, 272.

XVI. The Spectra of The Elements 273
1. Introductory, 273. 2. X-ray Spectra, 275. 3. Flame Spectra, 276. 4. Reversion Spectra, 278. 5. Phosphorescence Spectra, 278. 6. Arc Spectra, 280. 7. Spark Spectra, 282. 8. Regularities in Line Spectra, 282. 9. Line Spectra and the Periodic System, 285.

XVII. Chemical Affinity 289
1. Introductory, 289. 2. Hypotheses of Directed Affinity, 292. 3. Werner's Hypothesis, 295. 4. Friend's Views, 302. 5. The Abegg-Bodländer Hypothesis, 303. 6. The Electronic Hypothesis, 306. 7. Conclusion, 309.

XVIII. The Development of the Periodic Law 311
1. Early Attempts to Classify the Elements, 311. 2. De Chancourtois and Newlands, 315. 3. Mendeléef, 320. 4. Lothar Meyer, 324. 5. The Fulfilment of Mendeléef's Predictions, 326. 6. Other Confirmations of the Periodic Arrangement, 328. 7. Crookes, 329. 8. The Zero Group, 332. 9. Isotopes and Isobares, 334. 10. The Atomic Order and Atomic Numbers, 338.

XIX. The Atoms and the Periodic System 341
1. The Atomic Numbers and Atomic Properties, 340. 2. Some Resemblances not Expressed in the Periodic Table, 346. 3. The Rare Earth Elements, 353. 4. The Position of Hydrogen, 357. 5. Some Atomic Volume Problems, 358. 6. The General Arrangement of the Periodic Table, 362. 7. Surfaces Representing Periodic Properties, 368. 8. The Possibility of a Wider Periodic Generalisation, 369.

Digitized by Google

CHAPTER PAGE

XX. Some Views of Atomic Structure 373
1. Introductory, 373. 2. Some Points in Our Knowledge of Atomic Structure, 376. 3. Drawbacks of a Saturnian Atom, 381. 4. Bohr's Atom, 382. 5. Nicholson's Atom, 386. 6. The Lewis-Langmuir Atom, 389. 7. Noyes' Atom, 391. 8. Stewart's Atom, 394. 9. Conclusion, 395.

Bibliography 399

Appendix 403

Name Index 405

Subject Index 409

LIST OF PLATES.

I. Atomic Volume Curve . . . . . *At End*

II. Diagram Illustrating the Periodic Relations of the Elements . . . . . *At End*

III. The Periodic System . . . . . *Facing p.* 323

Fig. 30. Portion of Arc Spectrum of Iron . . . . „ *p.* 281

„ 38. { The Periodic Surface, Front View . . . . / „ „ „ Side View . . . . } „ *p.* 369

Digitized by Google

CHAPTER I.

INTRODUCTION.

THE present volume is not intended to survey the whole field of physical chemistry, nor does it even profess to describe all the more interesting parts of the subject: for any attempt to carry out either of these plans would have expanded the book far beyond the limits which seem desirable. The intention has been rather to select for treatment several interesting branches of physical chemistry and to throw some light upon their general outlines, in the hope that the descriptions given may arouse the interest of the reader sufficiently to make him consult the original literature or to look up other books in search of further information.

Written on this plan, the book has taken the form of independent chapters each of which deals with a particular subject: but, though the material is treated in this manner, the volume as a whole still possesses a certain connected thread of interest, and the order of subjects has been chosen so as to bring out this relationship between them. It may be well to give some idea of this underlying continuity in the text.

Physical chemistry may be described as a science which deals with (*a*) the relations between the physical properties of substances and their chemical constitution; and (*b*) the influence of external physical conditions on the course and result of chemical action. This is, perhaps, not a full definition of the field, but it covers the major and most important part of the subject.

Now, pure chemistry is concerned mainly with what may be termed the "quantity factor" in the operations of chemical affinity. It rests on the foundation of the doctrine of valency and its fundamental concern is with the proportions in which certain elements unite with one another. Superimposed upon

Digitized by Google

this, the idea of chemical structure has arisen, which has so thoroughly justified its existence in the field of organic chemistry.

Physical chemistry, on the other hand, takes into consideration the "intensity factor" in chemical operations: in addition to the mere mass-relations involved in a reaction, there is "reactivity," which expresses the velocity of chemical change, and this subject lies within the scope of physical chemistry. A concrete example will serve to make the matter clear. The methods of pure chemistry, when applied to the problem, inform us that one gramme-molecule of hydrogen will enter into combination with either one gramme-molecule of chlorine or one gramme-molecule of iodine. When the methods of physical chemistry are applied, we learn that the rate of combination between hydrogen and iodine is much slower than that between hydrogen and chlorine under the same conditions. Evidently, then, although in each case there are two gramme-molecules reacting with each other, the forces at work are more powerful in the case of chlorine than in the case of iodine, since the reaction with chlorine is much the swifter of the two. Thus through the study of reaction-velocities we are brought to consider the different modes of action of chemical affinity, even when monovalent atoms are compared with each other.

The study of chemical affinity brings to light the existence of something which appears to be analogous to potential energy, for though normally it lies dormant, yet in proper conditions it can be drawn into action and utilised. This force is termed *residual affinity*.

Another branch of physical chemistry deals with the relations between chemical constitution and the physical properties of substances; and it is found that this residual affinity which certain molecules possess has the power of influencing many of the physical properties of the compounds in which it exists. The next chapter of this volume is devoted to tracing this relationship, so as to bring out the extent of the influence exerted by this "potential" store of chemical affinity in the molecule.

The existence and influence of residual affinity having been thus established, it is of interest to look further afield

Digitized by Google

among chemical compounds and see whether traces of its presence cannot be detected by other methods. It is natural to turn first to the case of double salts; for in this section of chemistry we find two apparently saturated molecules uniting together to form a new material, the physical properties of which are different from those of either of its components, although the reactions of the new substance are identical with those of the compounds from which it was formed. Examination of the properties of these double salts brings to light the fact that in the double salt the two components are very feebly attracted to each other, the forces maintaining their union being apparently much weaker than ordinary chemical affinity. This subject forms the basis of Chapter III.; and Chapter IV. deals with some of the problems involved in the formation of double salts in Nature and the conditions of equilibrium between them.

Having thus been brought to consider the case of two molecules combining to form a loose association, it is natural to pass to another case of molecular union—complex salt formation—in which by the combination of two or more molecules a new material is formed having chemical properties entirely different from those of either of its component parts. When this field is investigated, it is found that the union of molecules has destroyed the original ionic character of the materials and has brought into existence a new type of ion—the complex ion. The methods of establishing the presence and determining the nature of these complex ions form the subject of Chapter V.

By this road we have been brought to a consideration of the phenomena of ionisation, and it is a short step to the consideration of another type of electrolytes: the pseudo-acids. In them it is found that the power of ionisation is not inherent, but that before they can dissociate electrolytically they must undergo a certain change in character. An account of the researches in this field occupies Chapter VI.

Consideration of the pseudo-acids leads directly to an examination of the indicators, which belong to the pseudo-acid class: and some account of the chemistry of indicators is therefore given in Chapter VII.

Hitherto in the volume, attention has been confined to

Digitized by Google

the behaviour of the solute, but at this point the action of the solvent comes under inspection. Although water is the commonest solvent in which electrolytic dissociation is observed, it is only one of many such media. Liquid ammonia and many other inorganic liquids also display dissociating power and yield solutions which conduct electricity. This section of the subject has been deeply studied by various workers; but Walden has extended the investigation to include a comparison between the chemical constitution of liquids, their dissociating power and many of their physical properties. This series of researches is described in Chapter VIII.

In the foregoing subjects, attention has been concentrated upon the problems of true solution; but a survey of this branch of the subject would be very incomplete without some reference to colloidal solutions; and this carries in its train the question of coagulation and the formation of gels. Chapter IX. has been devoted to a general description of the field of colloid chemistry.

The subject of colloids brings us to the Brownian movement which is shown by the particles in colloidal solution. Here, by a somewhat unexpected path, we reach a consideration of the kinetic theory of gases and find experimental support for this theory, which was lacking until the study of colloidal solutions was taken up with modern experimental refinements. This aspect of the subject is dealt with in Chapter X.

Since colloidal solutions merge on the upper limit into suspensions, the latter subject follows naturally in the sequence. The work of Perrin has shown that gross particles of gamboge suspended in a liquid behave exactly as molecules are supposed to behave in the gaseous state; and in this way a "visible proof" of the accuracy of the kinetic theory of gases has been attained after many years of vain attempts. This series of investigations forms the subject of Chapter XI.

The study of emulsions has not been limited in its results to supporting the kinetic theory, however, it has even led to the determination of the number of molecules which are present in a gramme-molecule of any compound. This number, Avogadro's constant, has recently been determined with wonderful accuracy by many different methods, some account of which is given in Chapter XII.

Digitized by Google

Leaving this branch of the subject, a return may be made to colloids from which we started, and a fresh field of research opens up in the phenomena of adsorption. Here we have to deal with the influence of surface action as distinct from mere absorption or solution. A short description of adsorption phenomena is given in Chapter XIII.

Finally, to close the field with which we began, Chapter XIV. contains a brief summary of certain theories of the colloid state which have been suggested from time to time. None of them is sufficient, but they form a very instructive example of how the same subject may be approached from different directions.

Chapter XV. deals with catalysis in some of its manifestations, and to a certain extent it hinges on to the chapter on adsorption.

This closes one section of the book. In the remainder of the volume, the subjects form a group by themselves, though there is still a link between the two sections formed by the problem of chemical affinity.

In Chapter XVI. a short account of emission and phosphorescence spectra is given, as part of this subject must be understood if the later chapters are to be fully appreciated.

Chapter XVII. brings us back to the problem of chemical affinity with which the volume started; and at this point an account is given of various typical hypotheses which have been suggested from time to time as to the basis of the phenomena of chemical reaction. Here, again, the main object kept in view has been to exhibit the various modes of regarding the problem which have come to light from time to time.

From chemical affinity and valency to the Periodic Arrangement of the elements is an obvious step. Chapter XVIII. contains a description of the main stages in the development of the Periodic System from its inception to the present day. In this, an attempt has been made to apportion the relative contributions brought by each investigator to the common fund; and it will be found that the account differs considerably from that usually given in text-books. The Periodic Law represents one of the greatest of scientific generalisations and furnishes material for consideration in the most diverse regions of thought. In spite of all that has been written upon the subject up to the

Digitized by Google

present, it is manifest that the root of the matter has not yet been reached. Fortunately, the Periodic System differs from most other subjects of speculation, for time spent in pondering over it is never lost, since the more thought is given to it, the more solid information is acquired at the same time from a mere study of its intricacies.

In Chapter XIX. certain aspects of the Periodic Table are examined, with the object of bringing out clearly some points at which the Periodic System seems to require further investigation. It is too often assumed that the difficulties in our way are minor ones; and it seems advisable to indicate some of the defects of the Mendeléef Table, which is by no means free from grave blemishes.

Having considered the relations of the elements to one another, it seems well to conclude the survey by dealing with modern hypotheses of atomic structure and to indicate as clearly as possible where the modern views of the model atom fall short of perfection. This subject is described in Chapter XX.

In concluding this introduction, it may be well to mention a point which has been kept in view during the writing of the book. A volume of this kind is intended to encourage the reader to do two things: (1) acquire a knowledge of facts and (2) form his own opinions on the subjects treated, apart from the hypotheses suggested by other people. For this reason, wherever it has been possible, the facts have been kept entirely separate from any theories on the subjects. It cannot be too often impressed upon a student that it is only by forming his own individual views upon chemical problems that he can become really a master of the subject. By this it is meant that he should be intellectually satisfied that a theory is firmly based before he accepts it; he should not encourage himself to take refuge behind the fact that "So-and-so says it is true". It is not necessary to evolve new theories of one's own, but it is equally unnecessary—and much more undesirable—to accept blindly anything which happens to find its way into print on one side or other of a controversy.

Digitized by Google

CHAPTER II.

RESIDUAL AFFINITY AND SOME PHYSICAL PROPERTIES.

1. *The Meaning of Residual Affinity.*

WHEN a nitrogen atom is united with three hydrogen atoms to form a molecule of ammonia, its attractive powers are evidently not wholly satisfied, since it remains capable of holding in addition a further hydrogen atom and a chlorine atom in the molecule of ammonium chloride. Thus, although ammonia is a perfectly stable and well-defined compound, the nitrogen in it is not exerting to the full the power which it possesses of retaining atoms in combination. A trivalent nitrogen atom, therefore, is potentially capable of exerting more chemical affinity than it openly displays; it has a certain store of latent energy, just as a weight resting upon a table contains potential energy which is capable of development under proper conditions. To indicate this condition of the nitrogen atom, the term *residual affinity* is used.

Many other atoms are capable of possessing residual affinity. For instance, among the commoner elements, divalent oxygen and sulphur are capable of attracting extra atoms and becoming quadrivalent; phosphorus in the trivalent state has the potentiality of quinqevalence; monovalent iodine can yield trivalent derivatives; and in the case of carbon compounds the acetylenic and ethylenic series contain carbon atoms in a state which enables them to attach to themselves other elements. In all these cases, the atom, when in its lower stage of valency, must be regarded as the seat of residual affinity, as is proved by actual chemical reactions.

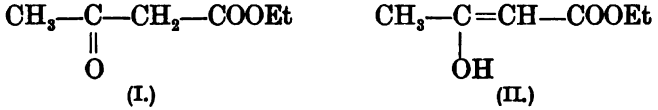
When a trivalent nitrogen atom is brought into the vicinity of another atom containing residual affinity, a reaction may occur if the conditions are suitable. But when the two atoms form part of the same compound already, it is possible that no

Digitized by Google

reaction between them will take place owing to spatial or other causes. None the less, the two centres of residual affinity may exercise a certain influence upon each other which is traceable in their behaviour. For example, the two radicles, —CO— and —NH_2, both contain residual affinity in the sense which has been defined above, since two hydrogen atoms can attach themselves to a carbonyl group and a molecule of hydrochloric acid can be attracted by an amino group. When these two groups are brought into close contiguity in an amide of an acid, such as R . CO . NH_2 it is found that each of them is influenced in its properties. The carbonyl group no longer shows the usual easy reducibility to —CH(OH)—; and the amino group loses its basic properties almost entirely. On replacing the carbonyl group by a methylene radicle, as in R . CH_2 . NH_2, we find that the amino group recovers its usual power of salt-formation; whilst the substitution of a methyl group for the —NH_2, as in R . CO . CH_3, restores to the carbonyl radicle all its powers of oxime formation, bisulphite compound formation, and cyanhydrin production which it had lost when in association with the amino radicle.

Thus by purely chemical tests it can be established that these two centres of residual affinity have influenced each other, although no actual chemical reaction has taken place between them. The state of mutual influence is termed *the conjugation of residual affinity*, or, more shortly, *conjugation*.

Acetoacetic ester will serve as an example of the next type of phenomena with which we must deal. This compound is known to exist generally as an equilibrium mixture of two materials having the structures shown below:—



(I.) (II.)

Investigation of the properties of these two substances proves conclusively that each of them is capable of adding on extra atoms; so that both of them contain residual affinity. The distribution of this residual affinity is not the same in the two molecules, however, for the compound (I.) reacts only very slowly with bromine, whereas (II.) unites immediately with bromine. Now when acetoacetic ester is prepared from its

Digitized by Google

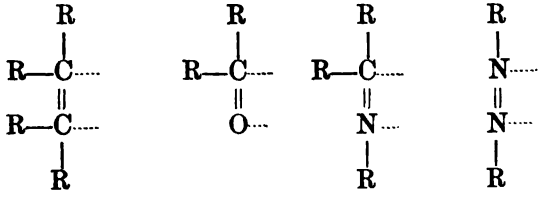
sodium derivative, it is found to be a mixture of (I.) and (II.); and the relative quantities of the two forms present can be altered by a change in the physical conditions under which the mixture is kept. But from the evidence just given, it is clear that this conversion of one form into another must be accompanied by a redistribution of the residual affinity in the molecule; so that it is definitely established in this way that *a rearrangement of residual affinity* can take place within a molecular structure.

In the foregoing paragraphs the subject has been kept on the firm basis of experimental results; and it is clear that the hypothesis of residual affinity is, if not the only one, at least the simplest which can be utilised to account for the facts.

2. *Thiele's Theory of Partial Valencies.*

In the last section, some examples were given of the mutual influence which two centres of residual affinity in the same molecule can exert upon one another. Up to the present, the most general treatment of the question is that of Thiele,[1] who succeeded in bringing into accord a very large number of phenomena by means of his theory of partial valencies.

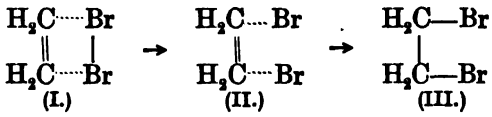
Thiele's views took their rise in the case of the double bonds which are used in many organic structural formulæ. Though these double linkages are written on paper as though they were composed of two separate single linkages, they are in practice weaker than an ordinary single bond such as is found in the ethane molecule; and to account for this Thiele assumed that when two atoms are united by a double bond, only part of their total available valency is thus employed; so that upon each atom there remains free a certain amount of affinity which he termed a *partial valency*. To symbolise this partial valency, he employed a dotted line thus:—



[1] Thiele, *Annalen*, 1899, **306**, 87.

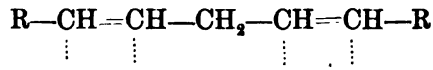
Digitized by Google

Thiele's conception of the mechanism of addition reactions is as follows: In the first place, the two reacting molecules approach each other as in (I.); thereafter the partial valencies come into operation, (II.); and finally, a rearrangement of affinity takes place which changes the partial valency into a normal single bond (III.).



On this basis, it is clear that the point of attack of an external atom upon an unsaturated molecule is represented by the partial valency; and the symbolical representation by means of the dotted line is really only a short way of expressing the experimentally established facts and can be employed apart from any theory at all.

Let us now turn to a case in which two unsaturated centres occur in the same molecule and again let us represent the doubly-linked atoms as having partial valencies:—



Owing to the two ethylenic linkages in this molecule, two molecules of bromine can be added on to the hydrocarbon; and it is found that if the bromine molecules be allowed to act one at a time the first product is a compound—

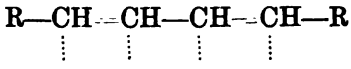
$$R\,.\,CHBr\,.\,CHBr\,.\,CH_2\,.\,CH:CH\,.\,R$$

which is then attacked by the second bromine molecule to yield the tetrabromo-derivative—

$$R\,.\,CHBr\,.\,CHBr\,.\,CH_2\,.\,CHBr\,.\,CHBr\,.\,R$$

This behaviour is perfectly normal.

When a molecule of the following type is examined—



its action with a single molecule of bromine might be expected to be the formation of the dibromo-derivative—

$$R\,.\,CHBr\,.\,CHBr\,.\,CH:CH\,.\,R$$

one of the double bonds being saturated and the other left

Digitized by Google

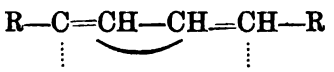
intact, just as in the previous case. In practice, however, this is not found. Instead of a single ethylenic bond being attacked by the bromine molecule, both the ethylenic linkages are attacked simultaneously and a *new* double bond is formed in the centre of the system :—

$$R—CHBr—CH : CH—CHBr—R$$

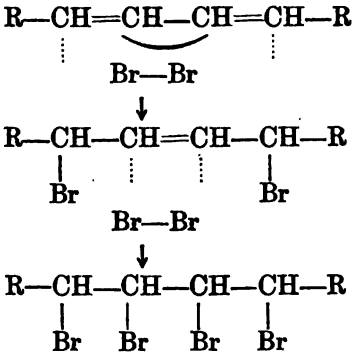
So far, the matter is entirely one of experiment, but it is now necessary to find some hypothesis which will account for the results. Since this apparently abnormal behaviour is observed only in cases where the two double bonds are separated from each other by two atoms joined by an ethylenic linkage :—

$$R—R=R—R=R—R$$

it is evident that this arrangement of valency has some peculiarity which is absent when more than one single bond is interposed between the two double linkages. To express the abnormal behaviour of such systems, Thiele writes the formulæ for them in this way :—



which represents the neutralisation of the two central partial valencies while leaving the exterior ones free to act. Thus the successive actions of two molecules of bromine upon such a molecule would be represented thus :—



A system of the type shown above, in which a single bond lies between two double bonds, is termed a *conjugated system*

Digitized by Google

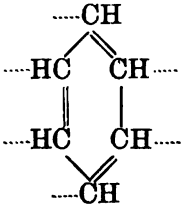
of double bonds, and, as has been explained, it is supposed to differ from a system of two isolated double bonds owing to a kind of mutual neutralisation of the two inner partial valencies. This neutralisation can be symbolised by assuming that the carbon atoms are alternately positive and negative in character in which case the system would assume the following form :—

$$R—\overset{+}{C}H=\overset{-}{C}H—\overset{+}{C}H=\overset{-}{C}H—R$$

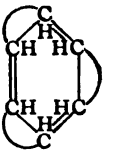
and it may be supposed that the two inner + and − charges neutralise each other, whilst leaving the exterior ones free to act.

It must be borne in mind that this system of conjugated double bonds may be influenced by residual affinity concentrations in other parts of the same molecule, so that in certain cases [1] the Thiele rule of addition does not hold good. But in general it appears to be a fair working guide to the behaviour of compounds which would seem abnormal upon the ordinary conceptions of affinity.

The most interesting application of Thiele's theory is to be found in the case of benzene. Using the Kekulé formula, benzene contains three double bonds, between each pair of which lies a single bond, so that if all the partial valencies are written in full it would be represented as in (I.). If now each pair of partial valencies be equated across a single bond, the formula assumed the form shown in (II.)—



(I.)



(II.)

Now in the form (II.), benzene evidently possesses no free partial valencies, since all of them are conjugated ; and this

[1] See on this question Thiele, *Annalen*, 1899, **306**, 89; 1900, **311**, 248; 1901, **319**, 129; Erlenmeyer, *ibid.*, 1901, **316**, 43; Vorländer, *ibid.*, 1902, **320**, 73; 1906, **345**, 206; Thiele and Häckel, *ibid.*, 1902, **325**, 6; Hinrichsen, *ibid.*, 1904, **336**, 182; Harries, *ibid.*, 1903, **330**, 225; Michael and Leighton, *J. pr. Chem.*, 1903, **68**, 521; Bauer, *ibid.*, 1903, **72**, 206; Flürscheim, *ibid.*, **71**, 503; Michael, *ibid.*, 1899, **60**, 467; 1903, **68**, 503; 1907, **75**, 1 .

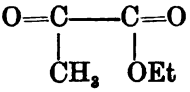
Digitized by Google

corresponds so closely to the inert behaviour of the benzene molecule during addition reactions that it furnishes a most valuable confirmation of Thiele's theory.

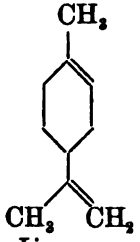
This influence of conjugation is traceable also when the intensity factor of chemical reactions is investigated. A comparison of the reactivity of the carbonyl groups [1] in acetone, lævulinic ester and pyruvic ester showed the following:—

Low reactivity	Lævulinic ester	$CH_3 . CO . CH_2 . CH_2 . COOEt$
Medium reactivity	Acetone	$CH_3 . CO . CH_3$
High reactivity	Pyruvic ester	$CH_3 . CO . COOEt$

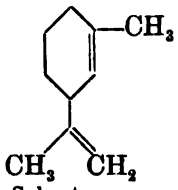
From this it is clear that the mere introduction of a carbethoxy group into the molecule has no stimulative influence, for when $—CH_2 . COOEt$ is substituted for one of the hydrogen atoms of acetone the reactivity of the carbonyl is actually reduced. On the other hand, pyruvic ester manifests a very high degree of reactivity. Examination shows that pyruvic ester is the only one of the three compounds which contains a conjugated system of double bonds:—



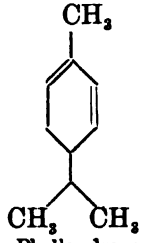
In thermochemical relationships, the same influence of conjugation can be traced. As can be seen from the formulæ below, limonene and sylvestrene contain isolated systems of double bonds, whereas the double linkages of *a*-phellandrene and carvenene are conjugated ones. The figures [2] below the formulæ give the heats of combustions in kilogramme-calories per gramme-molecule and inspection will show that the conjugated compounds have much lower heats of combustion than the isomeric non-conjugated substances.



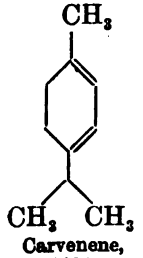
Limonene, 1466.



Sylvestrene, 1464.



a-Phellandrene, 1434.



Carvenene, 1424.

[1] Stewart, *Trans.*, 1906, **87**, 187; 1907, **89**, 489.

[2] Auwers, Roth and Eisenlohr, *Annalen*, 1910, **373**, 267.

Digitized by Google

From the foregoing evidence it is clear that the chemical character of a molecule is deeply influenced by the presence of a system of conjugated double bonds. In the following sections it will be shown that this abnormality is not confined to chemical properties alone, but is traceable also in many physical properties. In fact it seems to be the case that the presence of such a system in a molecule upsets all normal rules.

3. *Space-Conjugation.*

In the previous section, the mutual influence of two centres of unsaturation was considered in the case in which these two centres are adjacent in the *structure* of the molecule; but it is now known that structural propinquity is not absolutely

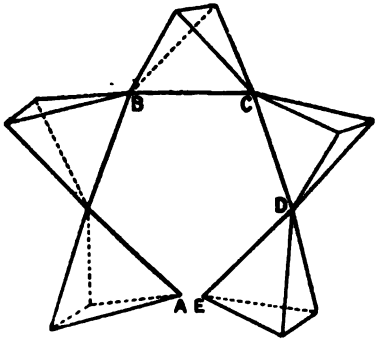


FIG. 1.

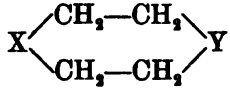
necessary in order that one centre may influence another. If the two centres of unsaturation be near together in space, even if they be structurally separated from each other by a chain of carbon atoms, they may still exert a traceable effect upon each other.

The tetrahedron of van't Hoff exhibits this state of affairs in the simplest manner of all. In the diagram (Fig. 1) the five tetrahedra represent a chain of five carbon atoms, the corners of the tetrahedra being regarded as the points of union of the atoms. It will be seen that although the carbon atoms at the two ends of the chain are *structurally* far-distant from each other, they are actually in the model very close together in space. Thus in any aliphatic chain the 1, 5 and 1, 6-positions may lie very near together, even though they are separated

Digitized by Google

from each other by three or four carbon atoms in the chain. This theoretical conception is fully justified by the readiness with which atoms in the 1, 5 and 1, 6-positions interact with each other, whereas atoms in the 1, 3 and 1, 4-positions show little tendency to interact.[1]

Again, in cyclic compounds, atoms in the positions 1 and 4 in a six-membered ring exert a mutual influence, although structurally they are not close to each other. Clarke[2] determined the reactivity of the groups X and Y in the six-membered system:—



where X and Y were atoms of oxygen and sulphur or the radicle = N . R. The results obtained may be summarised as follows. The nature of the group X has an influence on the reactivity of the group Y. If X and Y be the same, an enhancement of reactivity is observed; whilst if X differs from Y, the reactivity is diminished. It will be noticed that the oxygen atom, the sulphur atom and the group = N . R all contain residual affinity, since they are not exerting their full possible valency; so that the case is similar to the ordinary conjugation of structurally adjacent centres of unsaturation.

4. *Boiling-point Relations.*

The influence exerted upon the boiling-point of a compound by the presence of residual affinity within the molecule is a somewhat complicated one; and it will be necessary to deal with it from different points of view.

In the first place we may examine the effect produced when the quantity of unsaturation in the molecule is increased, while the situation of it remains unaltered. Corresponding compounds from the paraffin, olefine and acetylene series are classified below:—

$CH_3—CH_2—CH_2—CH_3$	B.P. +1°	$CH_3—CH_2—CH_2OH$	B.P. 97·4°
$CH_3—CH=CH—CH_3$	B.P. +1° / +2·5°	$CH_2=CH—CH_2OH$	B.P. 96°
$CH_3—C\equiv C—CH_3$	B.P. +27°	$CH\equiv C—CH_2OH$	B.P. 114°

[1] For a full account of these phenomena, see Stewart, *Stereochemistry*, 1919, pp. 170 ff.

[2] Clarke, *Trans.*, 1912, **101**, 1788; see also Clarke, Macbeth and Stewart, *Proc.*, 1913, **29**, 161.

Digitized by Google

These figures are sufficient to show that the presence of a single ethylenic linkage in a molecule exerts very little influence upon the boiling-point of the substance; but the extra unsaturation introduced by the change from the double to the triple bond has a very marked effect.

The acetylenic linkage has, of course, the power of attracting four halogen atoms, so that in quantity its additive capacity is equal to that of two ethylenic linkages. The concentration of the unsaturation in one spot, however, influences the boiling-point of the substance, as can be seen by comparing the following isomers:—

$CH_3—C\equiv C—CH_3$	B.P. +27°	$CH_3—CH_2—C\equiv C—CH_3$	B.P. 55°
$CH_2=CH—CH=CH_2$	B.P. −5°	$CH_2=CH—CH=CH—CH_3$	B.P. 42°

In such cases the acetylenic isomer has the higher boiling-point.

A comparison between the boiling-points of two isomeric compounds, one of which contains a conjugated system of double bonds whilst the other possesses only isolated double bonds, will suffice to show that as a general rule the conjugated substance has the higher boiling-point of the two. In making such comparisons, it is necessary to confine examination to cases in which the general structures are the same, since the occurrence of branched chains has an influence upon boiling-point. The following examples are free from any such complications; and it will be seen that the conjugated compound has a boiling-point considerably higher than its unconjugated isomer:—

	Boiling-point.
$CH_3 . CH : CH . CH : CH . CH_3$	87°
$CH_2 : CH . CH_2 . CH_2 . CH : CH_2$	61°
$CH_3 . CH : CH . C(=O) . CH_3$	121°
$CH_2 : CH . CH_2 . C(=O) . CH_3$	108°
$CH_3 . CH : CH . C(=O) . OH$	169° / 180°
$CH_2 : CH . CH_2 . C(=O) . OH$	163°

Digitized by Google

Thus the presence of a conjugated system of double bonds appears to enhance the cohesive power of a liquid to a very marked extent, as measured by the boiling-point.

5. *Refractivity.*

The optical properties of compounds are roughly divisible into two main classes: additive properties and constitutive properties. This division is, however, a somewhat arbitrary one; for all optical properties appear to be influenced by both the additive and constitutive factors, though the relative influence of these differs from property to property. Thus, in the main, the refractive index of a compound is obtainable by a summation of various constants, each of which corresponds to a particular part of the molecular structure of the compound under examination; and the approximation between theory and practice is generally a very close one.

The presence of isolated double or triple linkages in a substance raises the refractivity by a fixed amount, but when a conjugated system of double bonds exists in the molecule, the ordinary method of calculation breaks down; and the observed value of the molecular refractive power is found to diverge considerably from that calculated from the ordinary constants. This deviation is termed *optical anomaly*, and it may be either positive or negative in sign—*i.e.*, the calculated value may exceed or be less than the observed value.

One or two examples may be given in order to show the extent of the deviation which is produced by the presence of a conjugated system.

In the first place, the constants employed are the following. They hold good for the *a*-line in the spectrum and are calculated on the basis of the formula:—

$$\frac{n^2 - 1}{n^2 + 2} \times \frac{m}{d} = [R_L].$$

Here $[R_L]$ represents the molecular refraction; n is the observed refractive index; m is the molecular weight, and d the density of the substance under examination.

1 carbon atom	2·365
1 hydrogen atom	1·103
1 ketonic oxygen atom	2·328
1 hydroxylic oxygen atom	1·506
1 ethylenic linkage	1·836

Digitized by Google

In order to calculate the molecular refractivity of the substance diallyl, $CH_2 : CH . CH_2 . CH_2 . CH : CH_2$, on this basis, all that is necessary is to multiply the appropriate constants by the proper numbers and add up the resulting figures, as shown below :—

		$[R_L]_a$.
6 carbon atoms	2·365 × 6	= 14·190
10 hydrogen atoms	1·103 × 10	= 11·03
2 ethylenic linkages	1·836 × 2	= 3·672
Calculated for molecular refraction . .		28·892
Observed value [1]		28·77

It will be seen that in this case the calculated and the observed results differ only by a little over one-third per cent.

Now, since the substance 2, 4-hexadiene—

$$CH_3 . CH : CH . CH : CH . CH_3$$

contains exactly the same number of carbon atoms, hydrogen atoms and double bonds as diallyl does, we should find its calculated refractivity to be 28·892 also. When the observed value [2] is determined, however, it is almost a whole unit greater than this, *viz.*, 29·87. The only difference between diallyl and 2, 4-hexadiene lies in the fact that the latter compound contains a conjugated system which is absent from the structure of diallyl; and it is to the presence of this conjugated system that the optical anomaly must be ascribed, since there is no other possible origin.

Another example may be chosen from the carboxylic acids, so as to include all the constants given above; and in this case three isomeric substances [3] can be compared.

	$[R_L]_a$.	
$CH_3 . CH_2 . CH_2 . CH : CH . COOH$	31·56	Observed values.
$CH_3 . CH_2 . CH : CH . CH_2 . COOH$	30·99	
$CH_3 . CH : CH . CH_2 . CH_2 . COOH$	30·98	
Calculated value . . .	30·88	

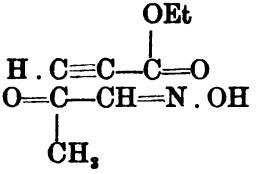
It can be seen that in the first compound there is a conjugated system comprising the ethylenic linkage and the carbonyl group of the carboxyl radicle; whereas no such conjugation is present in either of the other two molecules. The

[1] Brühl, *Ber.*, 1907, **40**, 881. [2] Brühl, *loc. cit.*
[3] Eykman, *Chem. Centralblatt*, 1907, II. 1205.

Digitized by Google

non-conjugated structures exhibit almost identical molecular refractivities, both of which are within about $\frac{1}{3}$ per cent. of the calculated value. The conjugated system, on the other hand, deviates from the calculated figures by three-quarters of a unit, or over 2 per cent.

It must be borne in mind that although the system of conjugated double bonds is one of the commonest, it is not by any means the only system which produces these anomalous effects. Whenever two centres of residual affinity come within each other's sphere of influence, similar results are obtained. The figures below illustrate this in the case of a system composed of a double and a triple bond between carbon atoms[1] and also in another system containing a carbonyl linkage and a double bond between a carbon and a nitrogen atom.[2]



	$[R_L]_a$ obs.	$[R_L]_a$ calc.	Difference.
H . C≡C—C(OEt)=O	25·12	24·62	0·50
O=C(CH$_3$)—CH=N . OH	21·39	20·39	1·00

It will be seen that the differences between the observed and the calculated values are here very marked.

In certain compounds the optical anomaly attains surprising dimensions. For example, in the case of diphenyl-hexatriene,[3] C_6H_5 . CH : CH . CH : CH . CH : CH . C_6H_5, the calculated molecular refractivity is 76·74 whilst the observed value is 100·9; so that the anomaly here is no less than 24·16 units, or about 30 per cent.

The case of benzene is curious but not inexplicable. The calculated value of the molecular refractivity is 26·31 whilst the observed value[4] is 25·93, so the anomaly has a minus value of 0·38. In view of the fact that benzene may be regarded as containing a system of three conjugated double bonds, this seems at first sight somewhat surprising; but further consideration will show that the result is not so abnormal as might be supposed. In all the cases hitherto chosen as examples in this section there have been, according to the Thiele theory, free

[1] Perkin, *Trans.*, 1907, **91**, 835.
[2] Muller and Bauer, *J. Chim. phys.*, 1903, **1**, 190.
[3] Smedley, *Trans.*, 1908, **93**, 376.
[4] Brühl, *Zeitsch. physikal. Chem.*, 1887, **1**, 349.

Digitized by Google

partial valencies at the *ends* of the conjugated systems; and in each of these cases there has been optical anomaly of a well-marked type. In the benzene ring, on the other hand, owing to the completeness of the conjugation, there is no free partial valency left at any point. Thus benzene stands in a class by itself and its refractive power could hardly be expected to follow the same rules as those which suffice for ordinary unsaturated substances.

6. *Magnetic Susceptibility.*

When bars of iron and of bismuth are suspended between the poles of an electromagnet, it is found that they swing into a position of rest at right angles to one another; and metals other than these exhibit the same kind of differences in their behaviour. Metals which comport themselves like iron are said to be paramagnetic, those which resemble bismuth are termed diamagnetic.

Not only elements but compounds also display this sensitiveness to the magnetic field's action; and measurements of the phenomena are obtainable by means of the following apparatus. A tube is placed vertically in a magnetic field and filled with the liquid under examination. On turning on the electromagnet which produces the field, it is found that the meniscus of the liquid either rises or falls in the tube. With the current on, the level of the meniscus is brought to a fixed point; after which the magnet is demagnetised; the liquid falls or rises slightly in the tube; and the new level is read off. The extent of the change gives a measure of the influence of the magnet upon the liquid.

Magnetic susceptibility is in the main an additive property, like refractivity; so that constants can be found for the atoms of various elements. Thus Pascal[1] assigned the following values to some of the commoner atoms: H = − 30·5; C = − 62·5; F = − 63·0; Cl = − 209·5; Br = − 319·2; I = − 465·0. In each case the constant is multiplied by 10^{-7}.

As in the case of refractivity, the value for oxygen varies according to the manner of its linkage. When combined with two hydrocarbon radicles, its constant is -50×10^{-7}, the

[1] Pascal, *Bull. soc. chim.*, 1911, **9**, 6.

Digitized by Google

minus sign showing that it is diamagnetic. In the carbonyl grouping of acids and esters it remains diamagnetic, but the numerical value becomes -13×10^{-7}. When existing in ketones or aldehydes, it is paramagnetic, with a value of $+66 \times 10^{-7}$.

The influence of conjugation is very well-marked in magnetic susceptibility. Normally, the correction for a triple bond is $+8 \times 10^{-7}$; and that for a double bond is $+57 \times 10^{-7}$. When more than one double bond is introduced into the molecule, however, the value becomes $+110 \times 10^{-7}$, so that clearly some disturbance has occurred which prevents the two separate bonds exercising their full influence.

Again, when an amido radicle is placed alongside a carbonyl group in the molecular structure, it is found that the carbonyl group ceases to exert its full influence. Thus in the monoamides, the value for the carbonyl group is $+32 \times 10^{-7}$; in the diamides and imides it is $+26 \times 10^{-7}$; and in urea it actually ceases to produce any effect at all.[1]

The subject has not been fully worked out, but these figures are sufficient to show that in its general lines magnetic susceptibility resembles refractive index in many respects.

7. *Magnetic Rotatory Power.*

When a liquid is placed in a strong magnetic field it becomes capable of rotating the plane of polarisation of a light-ray which is passed through it from a Nicol prism; and the degree of rotation is found to be closely connected with the chemical constitution of the liquid under examination.

In the case of refractivity, the measurements made are absolute measurements; but in the case of magnetic rotatory power it is found more convenient in practice to choose a standard substance and compare with it under the same conditions any compound which it is necessary to examine. Water is the standard substance employed in all the more important work which has been done in this field.[2]

[1] Pascal, *Bull. soc. chim.*, 1912, **11**, 111.

[2] Sir W. H. Perkin, *Trans.*, 1884, **45**, 421; 1886, **49**, 205, 777; 1887, **51**, 362, 808; 1888, **53**, 561, 695; 1889, **55**, 680; 1891, **59**, 981; 1892, **61**, 800; 1893, **63**, 57, 488; 1894, **65**, 20, 402, 815; 1895, **67**, 255; 1896, **69**, 1025; 1900, **77**, 267 1902, **81**, 177, 292; 1908, **83**, 1284; 1904, **85**, 1417; 1906, **89**, 608.

Digitized by Google

The molecular magnetic rotation (M) is obtained from the following formula :—

$$M[\omega] = \frac{a\lambda\delta m}{ald_\mu}$$

in which a is the rotatory power of the substance under given conditions, l is the length of layer of solution through which the light passes, m is the substance's molecular weight, and d its density; whilst the corresponding Greek letters represent the corresponding values for water. If both substance and standard be examined in tubes of equal length, the factors l and λ drop out and the expression becomes—

$$M[\omega] = \frac{a\delta m}{ad_\mu}.$$

The assumption is made that the substances are unassociated; and obviously if this were not the case it would be necessary to introduce the fraction m/d into the equation. In general, however, the expression given above works quite satisfactorily in practice.

Like refractive index, the magnetic rotatory power of a compound is in the main an additive property; but the method of calculation differs considerably from that employed in the case of refractivity. Instead of ascertaining the factor corresponding to each atom in a compound, it has been found more convenient to employ what are termed *series constants*. Each individual class of organic compounds has its own series constant; and when the magnetic rotation of a substance is to be calculated, the first step is to identify the series to which the compound belongs. Thereafter, if there be n carbon atoms in the substance, the molecular magnetic rotation can be obtained from the following formula :—

$$M[\omega] = S + n \times 1{\cdot}023$$

in which S is the series constant.

For example, suppose that it were necessary to calculate the molecular magnetic rotatory power of oenanthylic acid, $C_6H_{13}.COOH$, the procedure is as follows: The substance belongs to the fatty acids; and the fatty acid series constant is known to be 0·393. Oenanthylic acid contains seven carbon atoms, so that to the series constant must be added

Digitized by Google

7 × 1·023. This gives a total of 7·554, and the actually observed value is 7·552, which is very close indeed.

Sometimes, however, things are not quite so simple. For example, take the case of ethyl tartrate—

$$C_2H_5OOC . CH(OH) . CH(OH) . COOC_2H_5.$$

This substance might be regarded as belonging either to the class of dibasic esters like succinic ester—

$$C_2H_5OOC . CH_2 . CH_2 . COOC_2H_5$$

or to the derivatives of glycol, $CH_2OH . CH_2OH$. It is clear that some doubt might arise as to which series constant should be selected in the calculation. It has been found, however, that when a compound belongs to two different series, the best result is got by taking as a basis of calculation the mean of the two series constants. Thus, in the case of ethyl tartrate, the procedure would be as follows :—

Series constant of succinic esters	= 0·897
Series constant of glycols .	= 0·196
Sum of two constants .	= 1·093 ÷ 2 = 0·546
Value of 8 carbon atoms (1·023 × 8) . .	= 8·184
Calculated molecular magnetic rotation	= 8·730
Observed value	= 8·766

When the structure of the compound under examination is very complicated, the difficulty of the calculation is again enhanced; but it is not necessary here to discuss the matter.[1]

Magnetic rotatory power is more constitutive in character than refractivity, so that structural changes which do not affect the refractive index to any appreciable extent have a very marked influence upon magnetic rotation. In the case of refractive index, it will be remembered, the substitution of a double or triple bond for a single linkage had a fixed effect upon the refractivity, no matter from what class the compound was drawn; but in the field of magnetic rotation, as the figures below will show, there is no constant figure which can be assigned in the same way.

[1] A full account will be found in Smiles, *Chemical Constitution and Physical Properties*, 1910.

Digitized by Google

	M[ω]	Difference.
$CH_3.(CH_2)_2.CH_2.CH_2.CH_3$	6·670	
		+ 0·803
$CH_3.(CH_2)_2.CH{=}CH.CH_3$	7·473	
$(CH_3)_2CH.CH_2.CH_3$	5·750	
		+ 0·444
$(CH_3)_2C{=}CH.CH_3$	6·194	
$CH_3.CH_2.CH_2.CH_2.CO.CH_3$	6·522	
		+ 0·657
$CH{\equiv}C{-}CH_2.CH_2.CO.CH_3$	7·179	
$CH_3.CH_2.CH_2.CH_2.COOEt$	7·500	
		+ 0·629
$CH{\equiv}C{-}CH_2.CH_2.COOEt$	8·129	

Just as the presence of two conjugated double bonds produces optical anomaly in the case of refractive index, it is found that the introduction of a conjugated system into a molecule produces magneto-optical exaltation, the observed value for the rotatory power being greater than that which is to be expected. The range of compounds examined in this field is much smaller than in the case of refractive index; but the following example will be sufficient here:—

		M[ω]	Difference.
Hexane	$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3$	6·670	
			0·803
Hexylene	$CH_3{-}CH_2{-}CH_2{-}CH{=}CH{-}CH_3$	7·473	
			0·947
Diallyl	$CH_2{=}CH{-}CH_2{-}CH_2{-}CH{=}CH_2$	8·420	
			3·776
Hexatriene	$CH_2{=}CH{-}CH{=}CH{-}CH{=}CH_2$	12·196	

Inspection of the figures shows that the introduction of one ethylene linkage raises the rotatory power by 0·803. The introduction of two double bonds which are not conjugated with each other produces almost exactly twice the effect of the solitary double bond. It might, therefore, be expected that when a third double bond comes into the molecule it would merely result in a further proportional rise. Actually, however, the three double bonds are conjugated with one another in hexatriene and the result makes itself felt in the magnetic rotation which jumps nearly 50 per cent. in value.

Digitized by Google

8. *Optical Rotatory Power.*

The rotation of the plane of polarisation by substances having an asymmetric molecular structure was observed more than a century ago; but even now it is not possible to calculate the rotatory power of any given compound in the same way as the magnetic rotatory power can be ascertained theoretically. All that can be said is that if the space-formula of the substance be built up, activity is to be expected when that space-formula is not superposable upon its mirror-image.

Since the two phenomena differ so widely from each other in general character, it is not surprising that there is no clear parallelism between them when special points are examined. It has been shown that in the case of refractive index, the substitution of a double linkage for a single bond produces a definite change in the refractivity of a molecule; and in the case of magnetic rotation the same alteration in structure leads to a change in rotatory power, though the increment in this case is not a fixed one. When optical rotation is investigated, however, even this general rule fails; for it has been shown [1] that no conclusions can be drawn as to the influence which increased unsaturation in a molecule will exert upon the rotatory power of the molecule.

In the case of sulphur atoms, the calling into action of extra valencies seems to have a slightly depressing effect upon the rotatory power, as the following figures [2] show:—

		$M[\alpha]_D$.
Di-*l*-amyl sulphide	$(C_5H_{11})_2S$	42·67°
Di-*l*-amyl sulphoxide	$(C_5H_{11})_2SO$	37°
Di-*l*-amyl sulphone	$(C_5H_{11})_2SO_2$	34°

The introduction of a system of conjugated double bonds into a molecule, however, exerts upon optical rotatory power an influence almost as clearly marked as that which is observed in the cases of refractivity and magnetic rotation. Hilditch [3] has shown this in the following way. By examining the rotatory

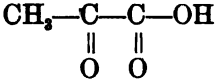
[1] Hilditch, *Trans.*, 1908, **93**, 1, 701; 1911, **99**, 208; Pickard and Kenyon, *ibid.*, 1911, **99**, 46; Rupe, *Annalen*, 1908, **327**, 157; 1917, **99**, 414; Haller, *Compt. rend.*, 1903, **136**, 788, 1222, 1613.

[2] Hilditch, *Trans.*, 1908, **93**, 1618.

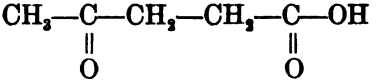
[3] *Ibid.*, 1888, 1618; 1909, **95**, 331, 1570, 1578; 1910, **97**, 1091; 1911, **99**, 224.

Digitized by Google

powers of a series of menthyl esters and brucine salts derived from the higher normal fatty acids, he arrived at a mean value which he designates as the "normal" value for the menthyl ester or the brucine salt. On comparing the deviations from this normal value in the cases of compounds containing conjugated double bonds and others in which the conjugation was destroyed by partial saturation, he found that the conjugated substances showed very much greater deviations. For example, pyruvic acid (I.) contains a system of conjugated double bonds whilst in lævulinic acid (II.) this conjugation is destroyed by the interposition of two methylene radicles:—



(I.)



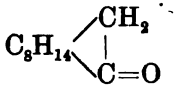
(II.)

The deviations from the normal value found by Hilditch in the case of the menthyl esters and brucine salts of these acids are given below:—

	Menthyl ester.	Brucine salt.
Pyruvic acid	+ 28°	+ 162·2°
Lævulinic acid	+ 11·8°	+ 71·9°

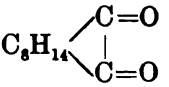
A similar result is found in the case of the camphor molecule; for the substitution of a carbonyl radicle for a methylene group leads to a very great increase in rotatory power:—

Camphor.



$[a]_D^{20°} = 55·2°$

Camphorquinone.



$[a]_D^{20°} = 113·2°$

Even space-conjugation may make its influence felt upon optical rotatory power. On examining the rotations of the menthyl esters of a series of dibasic acids, Hilditch[1] found the following values for the molecular rotation:—

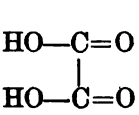
[1] Hilditch, *Trans.*, 1909, **95**, 1578.

Digitized by Google

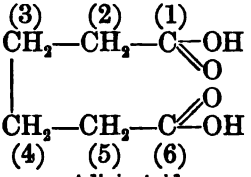
Menthyl ester of—	Molecular rotation.
Oxalic acid	– 330·6°
Malonic ,,	– 301·1°
Succinic ,,	– 322·7°
Glutaric ,,	– 328·3°
*Adipic ,,	– 353·6°*
Pimelic ,,	– 341·5°
Suberic ,,	– 331·1°
Azelaic ,,	– 337·2°
Sebacic ,,	– 320·6°

Inspection of these figures shows: (1) a very high value in the case of the oxalate; (2) a pronounced depression in the next three values; (3) a second maximum at adipic acid (marked with an asterisk); (4) an irregular fall after this point with alternations recalling those observed in the case of the melting-points of the acids.

In the case of oxalic acid, the high rotatory power can be accounted for by the presence in the molecule of two conjugated carbonyl groups. In the case of adipic acid, it is evident



Oxalic Acid.



Adipic Acid.

from the formula above that the two carbon atoms carrying residual affinity are in the critical 1, 6-position with regard to each other; and it seems not unwarranted to ascribe the high rotatory power to this association.

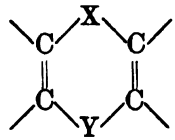
9. *Fluorescence and Luminescence.*

When a beam of light falls upon certain compounds, it is found that they glow in a characteristic manner as long as the exciting ray persists. The light which they emit is not due to reflection; for when the incident ray is polarised, the light emitted by the substance is found to be unpolarised; which appears to prove that it takes its origin within the molecules of the compound. A kindred phenomenon is observed when the vapours of certain organic compounds are subjected to the action of the Tesla discharge, under which they glow more or less brightly.

Digitized by Google

Neither of these phenomena has yet been treated quantitatively; but a connection has been traced between luminescent power and magnetic rotation; and some conclusions have been drawn which are of interest from the standpoint of residual affinity.

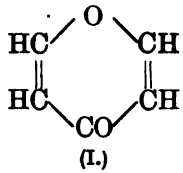
The first systematic study of the relations between fluorescence and chemical constitution was made by R. Meyer,[1] who found that the presence of certain groupings in the molecule went hand in hand with the power of fluorescence. For example, in the six-membered structure below



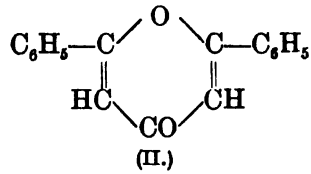
the following changes may, *inter alia*, be rung:—

X = C	X = C	X = C	X = C	X = N	X = N
Y = C	Y = O	Y = S	Y = N	Y = S	Y = O

Groups such as these are termed *fluorophores;* but in order that fluorescence may be exhibited, they need to be united with benzene nuclei. For example, pyrone (I.) shows no fluorescence, but diphenyl-pyrone (II.) is fluorescent in sulphuric acid solution:—



(I.)



(II.)

The presence of substituents has a marked influence upon fluorescent power. Thus fluorescein displays distinct fluorescence; dibromo-fluorescein has a much weaker power; and tetra-iodo-fluorescein exhibits no detectable fluorescence.

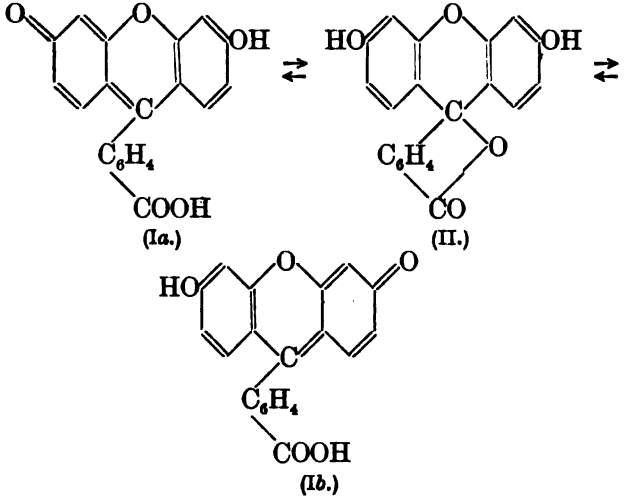
In the light of recent research, it seems most probable that the seat of fluorescence lies in the benzene rings and that the fluorophore groups merely serve to shift the wave-length of the light emitted from the ultra-violet up into the visible region of the spectrum.

[1] R. Meyer, *Zeitsch. physikal. Chem.*, 1897, **24**, 268; *Ber.*, 1898, **31**, 510; 1903, **36**, 2967.

Digitized by Google

No theory has been suggested which includes all cases of fluorescence; but Hewitt's hypothesis of double symmetrical tautomerism[1] suffices to account for a very large number of the known cases. According to Hewitt, a fluorescent substance occurs in two interchangeable forms, one of which is capable of absorbing the energy of the incident light and of changing into the second form during the absorption. The emission of the light-energy as fluorescence is then accompanied by the reconversion of the compound to its original structure.

A concrete example will make the matter clearer; and the case of fluorescein may be selected. Suppose that the substance exists in the form I*a*. By the action of light it may pass into the structure II. and thence into I*b*. The action is parallel to that of a pendulum which starts from an extreme point, I*a*., swings through its equilibrium-position, II., and then sweeps upward to its other extreme point, I*b*.



This theory of Hewitt is the only one which satisfactorily accounts for the fact that diphenyl-pyrone is non-fluorescent in neutral solvents but shows marked fluorescence in strongly acid solutions. In the one case, there is no possibility of double symmetrical tautomerism; but with the formation of an oxonium salt, the process becomes possible. Exceptions to Hewitt's

[1] Hewitt, *Zeitsch. physikal. Chem.*, 1900, **34**, 1; *J. Soc. Chem. Ind.*, 1903, **22**, 127.

Digitized by Google

theory have been found in certain cases, notably in the ultra-violet fluorescence of benzene, where no double symmetrical tautomerism is possible.

The Hewitt theory, however, suffices to bring out the fact that the production of fluorescence appears to be closely related to a series of rearrangements of residual affinity within the fluorescent molecule.

Turning now to the question of luminescence, it is found that two factors are requisite before this phenomenon can be displayed; a *luminophore* group containing a benzene ring and an auxochrome radicle such as $-N(CH_3)_2$, $-OH$ or $-NH_2$. When luminescence is shown, it is generally found that the compound exhibits marked reactive power, a readiness to yield a para-quinone on oxidation and anomalous optical and magneto-optical behaviour.

For the present purpose it will be sufficient to examine the last of these, since it is only in that case that quantitative measurements have been made. The magneto-optical quality of aniline will suffice as an example. The known value of the magnetic rotatory power of benzene is 11·284; and the constants for nitrogen and hydrogen are respectively 0·717 and 0·254; so that if it be assumed that no mutual influence occurs between the group C_6H_5 and the radicle $-NH_2$, then the magnetic rotatory power of aniline can be taken at the sum of these three numbers: 12·25. The observed value is 16·07, so that the anomaly, on this method of calculation,* is + 3·82

Now, when the anomalies of various benzene derivatives are calculated in this way and the results are then placed side by side with the luminescent power of the compounds, it is found that there is a remarkable general parallelism, as the following list shows:—

	Anomaly	Luminescent Power.
Nitrobenzene	− 2·15	None
Bromobenzene	− 0·09	None
Phenetol	+ 1·61	Weak
Aniline	+ 3·82	Strong
Dimethyl aniline	+ 8·59	Intense
Dimethyl-*p*-phenylene-diamine	+ 10·97	Very intense

* Note that this is not the true anomaly but represents the theoretical deviation of the benzene nucleus from its normal state on account of the presence of the amino radicle.

Digitized by Google

From these figures it is evident that when the anomaly is zero or a minus quantity, the luminescent power is negligible; whereas a positive anomaly is paralleled by luminescent power, the two properties increasing together. This suggests that luminescence is conditioned by the conjugation of the residual affinity of the phenyl group with that of the side-chain.

To test this, let us examine the cases of aniline and acetanilide. In aniline, the amino radicle has its full store of residual affinity which can act upon the phenyl nucleus; in acetanilide, on the other hand—as is clear from its chemical reactions—the entrance of the acetyl radicle has neutralised some of the free affinity of the nitrogen atom, so that it can exert less influence upon the phenyl radicle.

	Anomaly.	Luminescent Power
$NH_2—C_6H_5$	3·82	Strong
$CH_3—CO—NH—C_6H_5$ . . .	1·95	Weak

Thus the introduction of the acetyl radicle has lowered the anomaly and has reduced the luminescent power, just as might be expected from the theory. It therefore seems to be the case that the greater amount of residual affinity there is in the auxochrome group, the greater is its paralysing effect upon the phenyl nucleus and the greater the luminescent power of the compound.

Thus, although the quantitative investigation of luminescence is as yet in its infancy, enough is known to exhibit the influence which residual affinity exerts upon the phenomenon.

10. *Absorption Spectra.*

When the light of an iron arc is passed through a short column of a solution, two phenomena are possible. In the first place, it may be found that the transmitted light has been robbed of some of its rays in such a way as to leave a band of light which contains all the wave-lengths of the iron arc up to a certain point in the spectrum whilst all waves shorter than this have been absorbed by the liquid. In this case the phenomenon is one of *general absorption*. On the other hand, it may be found that the transmitted light has been selectively absorbed. For example, all the blue rays may have been absorbed by the liquid, whilst the spectrum on either side of the blue is still transmitted. In this case the spectrum of the

Digitized by Google

transmitted light will obviously not be continuous but will appear as a band of light interrupted at the region of the absorbed rays. Such a case is termed *selective absorption*. These two phenomena, general and selective absorption, are closely connected with residual affinity, as will now be shown.

Considering first the problem of general absorption, it is found that the introduction of unsaturation into a molecule tends to increase the absorptive power of the compound.[1] Fig. 2 shows the relative absorptive powers of succinic acid, HOOC . CH_2 . CH_2 . COOH, and the two stereoisomeric maleic

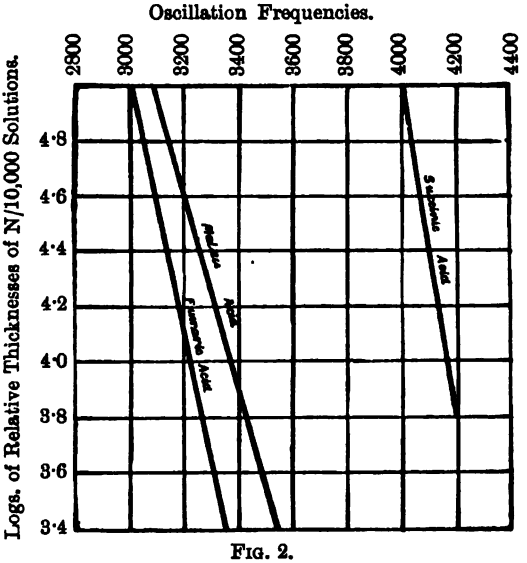


FIG. 2.

and fumaric acids, HOOC . CH : CH . COOH. Solutions of the three substances were examined in various layers of different depths and the ordinates represent the logarithms of the corresponding thicknesses of an N/10,000 solution whilst the abscissæ are the oscillation frequencies of the various lines in the complete spectrum. The red end of the spectrum is placed at the left, the ultra-violet at the right-hand of the diagram. The heavy black lines represent the demarcation between transmitted and absorbed light, all light to the right of them

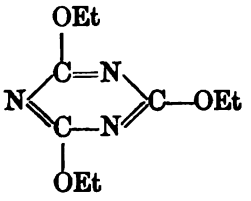
[1] Magini, *J. Chim. phys.*, 1904, 2, 403; Stewart, *Trans.*, 1907, 91, 199, 1537.

Digitized by Google

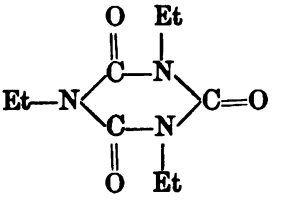
being absorbed whilst all to the left of them is transmitted. It will be seen that maleic and fumaric acids absorb very much more light than the corresponding saturated compound, succinic acid. Evidently, then, the presence of unsaturation in a molecule tends to increase its power of absorbing light. As in the case of optical rotatory power, the relative influences of double and triple bonds upon absorption spectra appear to obey no definite rule; for sometimes the double bond appears to exert a greater effect than the triple bond and *vice versa*.

It should be pointed out here that absorption spectra are so sensitive to constitutional factors that only a few attempts have been made to apply calculation to them.[1]

Turning to the question of conjugational influence upon general absorption, it is found that this is very strongly marked. For example, on comparing the general absorptive power of cyanuric and isocyanuric esters, it is found[2] that the normal compound (I.) is very much more absorbent than the iso-derivative (II.) :—



(I.)



(II.)

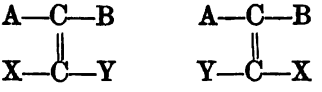
and from the formulæ it is evident that the one structure contains a series of conjugated double bonds, whereas the other has only three isolated carbonyl radicles. Examination of a large series of substances shows that this is a general rule, the conjugated compound being always more absorptive than the unconjugated isomer.[3] The influence of conjugated double and triple bonds has also been examined; but here it is found that constitutional factors seem to influence the problem considerably.[4]

The effect of space-conjugation has been traced among

[1] Henri, *Études de photochimie*, 1919.
[2] Crymble, Stewart, Wright and Rea, *Trans.*, 1911, **99**, 1262.
[3] Crymble, Stewart, Wright and Glendinning, *ibid.*, 451.
[4] Macbeth and Stewart, *ibid.*, 1917, **111**, 829.

Digitized by Google

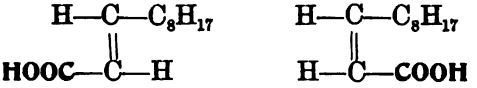
absorption spectra in the following way.[1] Stereoisomeric compounds of the type



were examined, and it was found that when A, B and Y were groups containing no residual affinity, then the general absorptive powers of the two isomers were almost identical. When A and Y were groups containing no residual affinity whilst B and X were centres of unsaturation, then the two isomers exhibited markedly different absorptive powers. This shows that in order to produce a difference in absorptive power between two isomers, the change of one isomer into the other must be accompanied by the shifting in the relative positions of two unsaturated centres; from which it seems clear that these two centres of residual affinity must influence each other to some extent, even though they are separated in the compound's structure and in space.

A concrete example will make the matter clear. In the change of citraconic acid into mesaconic acid, the two carboxyl groups (which are centres of residual affinity) are changing their relative positions; and in this case there is a marked change in absorptive power. In the case of erucic and brassidic acids, there is only a single centre of residual affinity in the molecule (apart from the central double bond), so that no such alteration in the relative positions of two unsaturated groups takes place; and, in consequence, the transmutation of erucic into brassidic acid involves very slight change in general absorptive power.

Citraconic acid. Mesaconic acid.



Erucic acid. Brassidic acid.

The residual affinity centres are indicated by heavy type in the formulæ.

[1] Macbeth, Stewart and Wright, *Trans.*, 1912, **101**, 599.

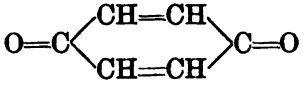
Digitized by Google

It is now necessary to turn to selective absorption and see what influence residual affinity produces in this field. In the first place, it is found that selective absorption is produced only when a molecule contains at least one centre of residual affinity. Acetone, containing the double linkage of the carbonyl group, $CH_3 . CO . CH_3$, exhibits an absorption band in the ultra-violet region of the spectrum; but when two hydrogen atoms are added on to the molecule, producing isopropyl alcohol, $CH_3 . CH(OH) . CH_3$, the power of selective absorption is lost and the compound shows only general absorption throughout the photographic spectrum.

The influence of conjugation makes its appearance very markedly in the case of selective absorption. Acetone, as has been said, has an absorption band in the ultra-violet. Acetonyl-acetone, $CH_3 . CO . CH_2 . CH_2 . CO . CH_3$, has a band in exactly the same region of the spectrum. But when the two carbonyl groups are brought into juxtaposition, as in diacetyl, $CH_3 . CO . CO . CH_3$, so that a conjugated system of double bonds is produced in the molecule, the band in the ultra-violet is replaced by a band in the visible region,[1] to which diacetyl owes its yellow colour. The introduction of a third carbonyl group in proximity to the other two brings the band still further toward the red end of the spectrum, so that the colour deepens.

$CH_3 . CO . CH_3$	Colourless.*
$CH_3 . CO . CO . CH_3$	Bright yellow.
$CH_3 . CO . CO . CO . CH_3$	Orange.

The dicarbonyl system yields an example of space-conjugation in the case of quinone—



In this compound the two carbonyl groups are obviously separated from each other structurally, yet the absorption band of quinone[2] is exactly like that of diacetyl; which seems to show that the quinone carbonyls, though apparently far apart

[1] Baly and Stewart, *Trans.*, 1906, **89**, 502. [2] *Ibid.*

* The absorption band in acetone does not affect our eyes, since we cannot appreciate ultra-violet rays.

Digitized by Google

in the structure, are yet near enough in space to influence each other just as the two carbonyls in diacetyl do.

An interesting example of conjugation[1] is furnished by some iodine derivatives; for here the unsaturated centres are the iodine atoms and not radicles like the carbonyl group.

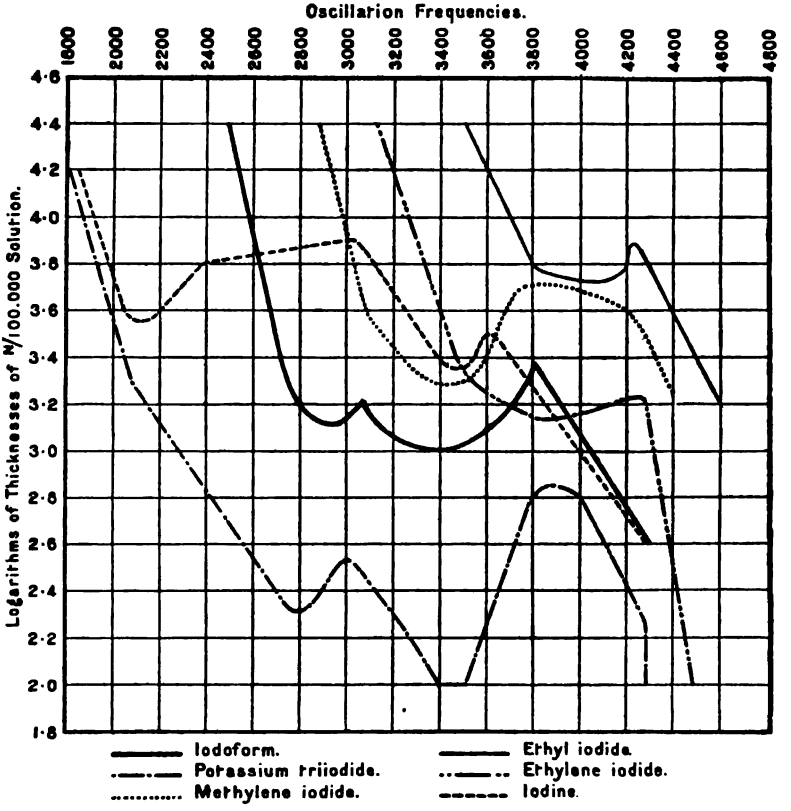


FIG. 3.

Examination of the absorption curves shown in Fig. 3 will show that there are three bands in the spectra of alkyl iodides, these bands having their heads respectively at the frequencies 4000, 3400 and 2900 approximately. The following table shows the relations between the various compounds:—

[1] Crymble, Stewart and Wright, *Ber.*, 1910, **43**, 1183.

Digitized by Google

Band occurs at a frequency of

4000	3400	2900
$CH_2(I)-CH_2-CH_2(I)-CH_2(I)$	$CH_2(I)(I)$	
	$CH(I)(I)(I)$	$CH(I)(I)(I)$
	KI_3	KI_3

It appears from this that the band at 4000 is characteristic of one iodine atom, either alone or separated from others by at least two carbon atoms. The band at 3400 is produced when two iodine atoms are attached to the *same* carbon atom. Finally, the third band at 2900 occurs only when there are three iodine atoms closely associated together in the molecule.

Turning to a more general problem, the relationship between valency and absorptive power may be touched upon.[1] Taking as a standard a 10-millimetre thickness of a normal solution of a salt (or a length of solution containing the equivalent quantity of a metallic ion), Crymble classed as "diactinic," or non-absorptive, those compounds which transmit light up to a wave-length 2300. Under this definition, metallic ions may be grouped into the following categories:—

A. Non-absorptive ions: Li, Na, K, Be, Mg, Zn, Cd, Ba, Al and Th.

B. Ions showing only general absorption: Hg, Tl, Sn, Pb, Sb and Bi.

C. Ions showing selective absorption: Cu, Ce, Mn, Fe, Au, Cr, U, Co, Pt, Ti and V.

Inspection will show that all the metals placed in Class A have a fixed valency; metals in Class B are capable of changing their valency, but only by *even* increments (*e.g.*, divalent tin to quadrivalent tin or monovalent thallium to trivalent thallium); whilst metals of Class C change their valency by *odd** increments (*e.g.*, divalent to trivalent iron, trivalent to quadrivalent cerium). It seems not impossible that here in the atoms of the elements there is something equivalent to the differences found in organic compounds. Two ethylenic

[1] Crymble, *Proc.*, 1911, **27**, 68.

* Gold appears to be an exception to the rule.

Digitized by Google

linkages produce general absorption in a molecule, whilst two conjugated carbonyl radicles give rise to selective absorption; and it may be that in the atomic structure there may be centres of affinity which behave in an analogous manner with regard to light.

11. *Conclusion.*

The foregoing pages contain sufficient evidence, drawn from many very different fields, to show the far-reaching influence which residual affinity exerts upon the physical properties of compounds. No attempt has been made to indicate all the properties which are affected by this factor, for a full treatment of the subject would occupy too much space; and it must not be supposed that all the effects of residual affinity have been dealt with in the previous sections of this chapter.

There is another problem which hinges directly upon residual affinity, and that is the question of the relative intramolecular motions of groups of atoms. It can hardly be assumed that the molecules of a liquid contain rigid arrangements of atoms such as Bragg has shown to exist in the solid state; and even in crystals it is possible that the atoms are in motion about certain mean positions. Any such intramolecular movements will naturally entail changes in the mutual influences exerted upon each other by the various centres of residual affinity within the molecule; so that we should expect to find some indications of this in the physical properties of substances. In some of the grosser properties, this action is manifest; for the lessening of cohesion which is observed when the temperature is raised can readily be accounted for on the hypothesis of residual affinity coupled with that of intramolecular vibration.

Yet another field of inquiry suggested by the residual affinity question is concerned with the relation between additive and constitutive properties. Why, for example, is refractive index so closely additive, whilst absorption spectra appear to be almost entirely constitutive properties? The more this question is pondered, the vaster the field appears which is open to research in this direction.

Digitized by Google

CHAPTER III.

DOUBLE SALTS.

1. *Introductory.*

THE complications to which even the simplest chemical processes may give rise are well illustrated by dissolving two substances in a solvent and subsequently allowing the solution to evaporate until crystals are produced. In the case in which the two solutes are organic compounds, or salts containing a common ion,* there are four possible results.

1. The two solutes may separate from the solvent in the form of independent crystals, so that it is possible to divide the one substance from the other by purely mechanical means. In this case the material is termed a *conglomerate.* For example, if a mixture of sodium chloride and sodium nitrate be crystallised from solution, two sets of crystals are produced, one of which contains only sodium chloride whilst the other set is composed solely of sodium nitrate.

2. The crystals which are deposited may each contain both solutes in quantities depending upon the percentage and solubility of each solute present in the solution. In this event, no mechanical separation can be effected, as each individual crystal contains a mixture of both solutes. If the crystals be redissolved in fresh solvent which already contains a certain amount of one of the solutes dissolved in it, then on evaporation a fresh set of crystals will be obtained which will have a composition different from that of the first set. A crystalline material of this type, in which the two solutes are not necessarily present in simple molecular proportions, is said to be a *solid solution.*† An interesting case of solid solution is

* This case is chosen to avoid the complications arising from the chemical interactions of four different basic and acid ions.

† The term *mixed crystals*, derived from the German *Mischkrystalle*, is sometimes applied to solid solutions; but its use is to be avoided, as it suggests the idea of a conglomerate.

Digitized by Google

furnished by the chlorates of thallium and potassium.[1] To a strong solution of thallium chlorate, some potassium chlorate is added; and the liquid is then allowed to evaporate. The crystals which are deposited contain both chlorates, the thallium chlorate being in excess. If greater and greater quantities of potassium chlorate be added to the solution before evaporation, larger and larger proportions of potassium chlorate make their appearance in the crystals. When the proportion of potassium chlorate in the solid solution reaches 36·3 per cent., a second set of crystals makes its appearance in which the proportion of potassium chlorate is 98 per cent. It is evident that this is analogous to the solution of phenol in water; and that the two sets of crystals represent respectively a solid solution of potassium chlorate in thallium chlorate and a solid solution of thallium chlorate in potassium chlorate.

3. As in the last case, the crystals deposited from the solution may each contain both solutes; but here re-crystallisation from a solvent containing one of the solutes produces no alteration in composition. Further, the two solutes are present in the crystal in simple molecular proportions. If the solutions of these crystals exhibit all the reactions of the two parent solutes, a *double salt* has been formed. The case of the alums will suffice to illustrate these phenomena. When potassium and aluminium sulphates are allowed to crystallise together from solution, crystals are produced which have the composition corresponding to K_2SO_4, $Al_2(SO_4)_3$, $24H_2O$. Further re-crystallisation of these alum crystals from a solution containing potassium sulphate does not lead to any alteration in the chemical composition of the alum, though some potassium sulphate crystals may be deposited as well from the liquid. It will be seen that in the alum the potassium sulphate and aluminium sulphate are present in simple molecular proportions. Finally, when the alum crystals are redissolved in water, the solution will give the ordinary tests for potassium, aluminium and sulphate ions, and will show no new properties.

4. Crystals may separate from the solution and on analysis may be found to contain both solutes in simple molecular proportions; but if these crystals when redissolved in the solvent are found to yield a solution having chemical properties dif-

[1] Roozeboom, *Zeitsch. physikal. Chem.*, 1891, 8, 504, 530.

Digitized by Google

ferent from those of either of the original solutes, the case is one of *complex salt* or *molecular compound* formation. Thus, when cobaltous cyanide and potassium cyanide are dissolved in water and the solution is treated with alcohol, amethyst-coloured crystals are produced which have the composition $K_4Co(CN)_6$. This potassium cobaltocyanide shows none of the ordinary cobalt or cyanide reactions but instead exhibits an entirely new series of chemical properties. It is therefore a complex salt.

The phenomena of double salt formation will be dealt with in the present chapter; and here it may be well to indicate some points of interest which suggest themselves in this connection.

In the first place, owing to their many points of resemblance, double salts and the hydrates of certain other salts may be classified together, the hydrates being regarded as double salts in which one of the constituents is water. This brings to light a question which illustrates the importance of double salt formation from the point of view of chemical affinity. Under our ordinary assumptions as to valency, sodium sulphate is a saturated compound, for all its atoms are exerting their full normal affinity. None the less, it is capable of combining with no less than ten molecules of water to form the deca-hydrate, which is a well-defined crystalline material. Evidently, then, in addition to our ordinary valency conceptions we must introduce a further idea of chemical affinity which will enable us to account for the production of these hydrates and double salts.

It is possible to assume that the double salt or hydrate may come into existence through the exertion of valencies which normally play no part in our formulæ. Thus the oxygen atom in a water molecule is represented only as di-valent, whilst actually we know that oxygen may exist in the quadrivalent state. Similarly, the union of the oxygen and sulphur atoms in sodium sulphate is represented by a double bond; and this junction may not utilise all the available affinity of the two atoms, leaving some attractive power still in reserve.

In any case, however, the main point of interest is the apparent feebleness of the attractive forces in the case of

Digitized by Google

double salt formation; for, as will be seen later, a mere change of temperature through a slight range is sufficient to render the double salt incapable of stable existence. Solvent action also has a marked influence upon the stability of double salts. The very slight variations in external conditions which thus bring about deep-seated changes in the chemical composition of double salts make the matter one of no little interest from the point of view of chemical affinity.

The relations between double salt formation and crystalline character are too obvious to require more than a passing mention, for the case of the alums is well known. Here, again, the influence of external conditions is very marked; for the phenomena of deliquescence and efflorescence show that slight changes in the pressure of water-vapour in the air surrounding certain salts are sufficient to alter the physical nature of the materials beyond recognition, owing to the destruction of the crystalline character. Further developments in our knowledge of the relation between double salt formation and crystalline structure may be expected from the application of the X-ray method of crystal analysis.

2. *Some Chemical Factors Influencing Double Salt Formation.*

It has already been pointed out that the power of forming double salts is not possessed by all compounds. The chemical nature of the ions from which the salts are produced appears to be a factor of importance in the matter. Thus magnesium sulphate and ferrous sulphate do not combine to form a double salt but yield a conglomerate instead; yet ferrous sulphate and ammonium sulphate give rise to Mohr's salt—

$$(NH_4)_2SO_4 . FeSO_4 . 6H_2O.$$

Evidently the substitution of ammonium for magnesium suffices to call the power of double salt formation into existence. Again, from zinc sulphate and copper sulphate no double salt is obtainable, despite the well-known capacity of copper salts to yield complex compounds; but zinc sulphate and potassium sulphate produce the double salt having the formula—

$$ZnSO_4 . K_2SO_4 . 6H_2O.$$

Digitized by Google

The acidic radicles also show similar phenomena; for while sodium chloride yields no double salt with sodium nitrate, the latter compound forms a double salt with sodium sulphate.

Atomic weight appears to have some influence upon the formation of double salts.[1] When ferric chloride is crystallised from a solution containing chlorides of the alkalis, it is found that sodium chloride forms only a series of solid solutions with the ferric salt; potassium chloride at 21° produces a double salt having the composition: $FeCl_3 . 2KCl . H_2O$; whilst at the same temperature caesium chloride yields two different double salts having the compositions: $FeCl_3 . 2CsCl . H_2O$ and $FeCl_3 . 3CsCl . H_2O$. It appears from these results that increase in atomic weight throughout the same chemical family has a favourable influence upon double salt production.

According to Retgers,[2] double salt formation is not to be expected from two salts which form a series of solid solutions of varying composition; and, conversely, if two salts combine to produce a double salt, it is unlikely that solid solutions of the two salts in each other will be obtainable. For example, ferrous sulphate yields solid solutions with magnesium sulphate, but no double salt can be obtained from the two; whereas potassium and sodium sulphates give rise to a double salt but cannot be made to form solid solutions.

3. *Transition Temperatures.*

The influence of temperature upon the stability of double salts was brought to light by the work of Scacchi[3] upon optically active and racemic compounds, in the course of which he showed that when a racemate is crystallised at high temperatures no resolution into the two antipodes is obtained, whereas crystallisation at a low temperature results in the formation of a conglomerate containing crystals of the two optically active forms.

Investigations in this field by van't Hoff,[4] to whom we owe the main advances in our knowledge of the subject, showed

[1] Hinrichsen and Sachsel, *Zeitsch. physikal. Chem.*, 1904, **50**, 81.
[2] Retgers, *ibid.*, 1889, **3**, 289, 497, **4**, 189, **5**, 486; 1890, **6**, 193; 1892, **8**, 6.
[3] Scacchi, *Rend. Accad. Sci. Fis. Mat. Napoli*, 1865, 250.
[4] van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897.

Digitized by Google

that this behaviour is characteristic of all double salts and salt hydrates. There is a certain temperature—to which van't Hoff gave the name *transition temperature*—which marks the upper or lower existence-limit for a double salt or a salt hydrate. Each salt or hydrate has its own peculiar transition temperature. It must not be assumed that conglomerates always exist below and double salts above the transition temperature; for this is not the case. For example, the double salt leonite, $MgSO_4 . K_2SO_4 . 4H_2O$, exists only between 61·5° and 18°. Above 61·5° and below 18° crystallisation leads to the formation of magnesium and potassium sulphates in conglomerate form. Again, at temperatures below 92°, the double salt, $CuCl_2 . 2KCl . 2H_2O$, crystallises from solution; but above 92° only the separate copper and potassium chlorides appear. On the other hand, when a solution containing magnesium and sodium sulphates is evaporated below 22° the crystals formed are a conglomerate of the two sulphates; above 22°, however, the double salt astrakanite, $MgSO_4 . Na_2SO_4 . 4H_2O$, is produced on evaporation of the solution.

The dominating factor in the problem is, of course, the heat of change which is required to convert the simple salts into the double salt, or *vice versa*, at the transition temperature. According to Le Chatelier's theorem, at the higher temperature, that change will take place which is accompanied by the absorption of heat. If, therefore, the production of a double salt from its components is an endothermic reaction at the transition temperature, the double salt will be stable above the transition point; whereas, if the formation of the double salt be an exothermic process, then the double salt will be stable at low temperatures and its components will exist uncombined above the temperature of transition.

It may be noted that the characteristic of the transition temperature is the change of physical state which occurs as a system passes through the transition point; and this brings out the correspondence between the transition temperature of a double salt and the point of liquefaction of a gas or the melting-point of a solid. In some cases the physical resemblances between the two processes are very close indeed. When sodium sulphate decahydrate, for example, is heated to its transition temperature, so much water is liberated that the

Digitized by Google

solid sulphate dissolves in the extruded liquid; and the phenomena appear identical with those exhibited by a solid at its melting-point.

Turning now to the methods whereby the transition point of a double salt or a salt hydrate may be determined, it will be found that the most varied properties have been utilised as an index to show the occurrence of a change of physical state in the material. These methods may now be taken up in turn.

1. *The Dilatometric Method.*[1]—When a double salt is converted into its components, or *vice versa*, it is to be expected that there will be a sudden change in volume due to the alteration in constitution. If this volume change be sufficiently marked, it forms one of the simplest criteria of the transition

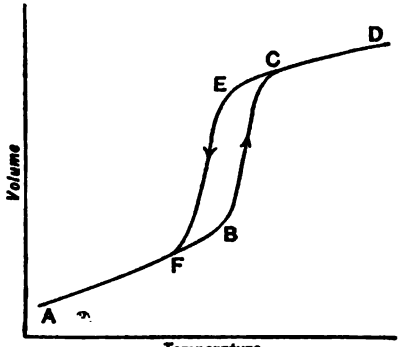


FIG. 4.
From Findlay's "Phase Rule".

temperature. The apparatus employed, the dilatometer, resembles a thermometer with a very large bulb. Into this bulb the double salt is introduced and is covered with oil. The level of the oil is read off on the graduated stem of the dilatometer just as we read off the height of mercury in a thermometer. The bulb of the dilatometer is now placed in a bath whose temperature is gradually raised. Readings are taken simultaneously of the bath temperature and the height of the oil level in the stem. At first, there will be a steady rise proportional to the temperature; but when the transition point is reached there will naturally be a rapid change in volume of the salt, quite independent of the normal increase in volume of the oil. Thus, on plotting the volume against

[1] van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897, p. 33.

Digitized by Google

the temperature, a break in the curve is obtained at the transition point. Since the transformation of a double salt into its components, or the reverse process, is not instantaneous, there is usually a slight lag in the volume increase. To allow for this it is best to make two sets of measurements, one with a rising, the other with a falling temperature. The two errors then counteract each other to some extent (Fig. 4). A modification of the method allows this lag to be turned to account. If a mixture of a double salt and the two components be placed in the dilatometer, they will not immediately come into equilibrium. The dilatometer bulb is therefore placed in a bath and allowed to attain constant temperature; after which readings of the oil level are taken as before. Now, unless the temperature of the bath is the transition temperature, it is obvious that the salt within the bulb will contract or expand in the course of time; for if the temperature is one at which the double salt is stable, then the components will be slowly changing into the double salt; or, conversely, if the double salt is unstable at the temperature of the bath, then it will be converted into a mixture of the components. In either case there will be a change in volume, which will make itself apparent in the alteration of the oil level in the stem. Suppose a contraction takes place. The temperature is noted and then the operation is repeated at other temperatures until some temperature is found at which expansion occurs. Now, at the transition temperature, since the components are there in equilibrium with the double salt, it is obvious that no change in volume can occur. Therefore the transition temperature lies between the temperature at which expansion occurs and that at which contraction is observed. By a series of measurements the limits between the two temperatures can be narrowed down and thus finally the transition temperature can be determined by a series of trials.

2. *The Tensimetric Method.*—The second method[1] of finding the transition point depends upon the fact that at the transition temperature, the vapour pressures of the double salt and its components must be in equilibrium. The apparatus usually employed is the Bremer-Frowein tensimeter as shown diagrammatically in Fig. 5. The whole apparatus is first

[1] van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897, p. 43.

Digitized by Google

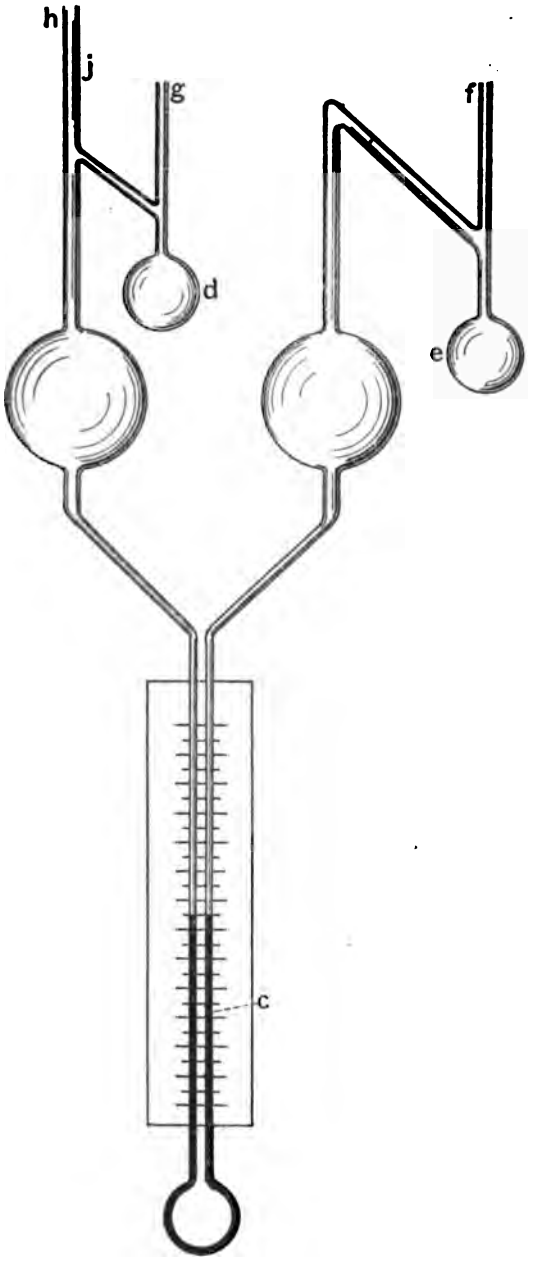


FIG. 5.

Digitized by Google

carefully dried, and then the two substances whose tensions are to be compared are introduced into *d* and *e* respectively. The substance having the greater vapour pressure is usually introduced into *e*. Olive oil is then passed into the U-tube *c* by means of a fine funnel until it stands about half-way up the U-tube on both sides. The tubes at *f* and *g* are next sealed off and a mercury pump attached to *h*. The whole apparatus is then evacuated. When the highest possible vacuum is produced, the mercury pump is removed by sealing off the tube at *j*. The apparatus is placed in an air bath and its temperature gradually raised. At the transition temperature the surface of the oil in the two arms will reach the same level. Of course this is only an outline of the method; numerous precautions must be taken and some corrections have to be applied in order to make it accurate.

3. *The Thermometric Method.*[1]—If the temperature of ice be allowed to rise slowly, it will be remembered that when it reaches 0° C. a thermometer immersed in it will remain constant until all the ice has melted. Applying the analogy between the transition temperature and the melting-point, another method of determining the transition temperature can be devised. It is only necessary to note the temperature at which a thermometer seems to lag when the mass of double salt surrounding it is slowly heated or cooled towards its transition temperature.

4. *The Spectrometric Method.*—The fourth method of determining transition points depends upon the change of colour which some salts undergo at the transition temperature. For instance, a concentrated solution of the two simple salts ferric chloride and potassium chloride is yellow at ordinary temperatures, but if it be raised to about 22° C., the colour changes to red, owing to the formation of the double salt $FeCl_3 . 2KCl . H_2O$. This method may be employed even in cases where there is no visible change of colour, by using a photographic spectroscope and noting the change in the ultra-violet spectrum.

5. *The Solubility Method.*[2]—At the transition temperature the solubilities of a double salt and its components become

[1] van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897, p. 55.
[2] *Ibid.*, p. 51.

Digitized by Google

equal; and this has been employed in some cases to determine the transition point of the system. If the solubility of each of the three substances (double salt and its two components) be plotted against the temperature throughout a given range, three curves will be obtained which will cut each other at a point. This point gives the transition temperature.

6. *The Electromotive Force Method.*[1]—It is well known that if two vessels containing different solutions of some salt be connected together by a tube which allows the liquid to pass from one vessel to the other an electric current is obtained by immersing electrodes in the two vessels and connecting them by means of a wire. The current passes in the cell from the weaker to the stronger solution. Take the case of the two hydrates of zinc sulphate: $ZnSO_4 . 7H_2O$ and $ZnSO_4 . 6H_2O$. Saturated solutions of each of these are placed in two separate vessels along with some solid salt, the two vessels are then connected by means of a tube bent in such a way as to prevent the action being disturbed by convection currents; then into each vessel a zinc electrode is dipped. The electrodes are connected by a wire, and a galvanometer is included in the circuit. At temperatures below the transition point, the salt $ZnSO_4 . 6H_2O$ is more soluble than the other, so that the solution of the latter will be weaker in zinc sulphate. Hence the current will pass in the cell from the vessel containing the heptahydrate to that containing the hexahydrate. As the temperature is raised, the solubilities of the salts in the two vessels approximate more and more to each other, and consequently the current passing becomes weaker and weaker. Finally, at the transition temperature, it ceases to flow.

7. *The Viscosity Method.*[2]—It has been shown that the viscosity of the solution of a racemate is less than that of the corresponding active antipodes, and the transition point can be detected by the break in the temperature-viscosity curve.

8. *The Conductivity Method.*[3]—Electrical conductivity may be employed for the determination of the transition

[1] van't Hoff, *Bildung und Spaltung von Doppelsalzen*, 1897, p. 48.

[2] Dunstan and Thole, *Trans.*, 1908, **93**, 1815.

[3] Compare Archibald, *Trans. Nov. Scot. Inst. Sci.*, 1891, **9**, 307; Jones and his collaborators, *Amer. Chem. J.*, 1897, **19**, 83,; 1899, **22**, 5; 1900, **25**, 349 Lindsay, *ibid.*, 1901, **25**, 62.

Digitized by Google

point in the following way. Using solutions as concentrated as possible, the conductivity of a mixture of two salts in solution is calculated and is then compared with the actual measured conductivity. If there is a difference between them, it tends to indicate that a double salt has been formed; and by carrying out the experiments over a range of temperatures some clue may be obtained as to the position of the transition point.

9. *The Indicator Method.*[1]—When any hydrate is heated to its transition temperature in presence of sodium carbonate, water is liberated, and thus a solution is formed which has an alkaline reaction owing to the hydrolysis of some of the carbonate. If, therefore, the dry hydrate be mixed with sodium carbonate and a trace of dry phenolphthalein before heating, the attainment of the transition temperature will be indicated by the reddening of the phenolphthalein in presence of the alkaline solution. The application of this method of transition-point determination is obviously restricted; but it appears to be quite accurate within its own field.

10. *The Density Method.*[2]—In cases wherein marked hydration or dehydration occurs at the transition point, it is possible by means of a delicate hydrometer to observe alterations in the density of concentrated solutions of the salts concerned. The temperature of the solution is gradually raised, the density is plotted against the corresponding temperature; and the graph shows a point of inflexion at the transition point.

4. *Transition Intervals.*

We must next examine the solubility relations which have been observed in the case of double salts and their components. The matter was touched upon in the last section when dealing with the determination of the transition temperature by means of solubility; but in the present section the question must be approached from a somewhat different point of view.

It was shown by van't Hoff and Müller[3] that the transition temperature of rubidium racemate is 40° C. Below this

[1] McKeown, *Chem. News*, 1920, **120**, 266.

[2] I am indebted to Miss Pearl Blair, M.Sc., for working out this method practically.

[3] van't Hoff and Müller, *Ber.*, 1898, **31**, 2206.

Digitized by Google

temperature the racemate exists; above it, the individual dextro- and lævo-tartrates. If equal weights of the dextro-tartrate and of the lævo-tartrate be placed in a vessel containing the same weight of water at 15° C., both tartrates will go into solution in equal quantity, since their solubilities are equal; and since there is not enough water present to dissolve them, part of each tartrate will remain as a solid phase. A complication now enters into the problem. As the tartrates go into solution they are converted into the corresponding racemate, which is the stable form below 40° C.; and this racemate is less soluble than the tartrates. Consequently, the solution will be able to take up more of the single tartrates than it can keep in solution when they have combined to form a racemate. As a result there will be a continual deposition of racemate to keep pace with the amount of tartrates taken up by the water. In this way the following successive steps take place: the solution of the two tartrates, their conversion into racemate and consequent supersaturation of the solution with racemate, leading to a deposition of crystals of the racemate: and this process will go on until all the tartrates have been dissolved.

This is a simple case, owing to the fact that the two components of the double salt have the same solubility; but we must now consider a more complicated problem, and we may choose the case of astrakanite, $MgSO_4 . Na_2SO_4 . 4H_2O$, as an example.[1]

In this case, the two components of the double salt have not the same solubility, and in the first place it is necessary to find the solubility of the two component salts, sodium sulphate and magnesium sulphate, in presence of each other. This is done by placing an excess of both salts in contact with water and agitating at constant temperature until equilibrium is established, after which the solution is analysed. In this way the following figures are obtained:—

I. Solid Phases: Magnesium Sulphate and Sodium Sulphate.

Temperature.	Na_2SO_4.	$MgSO_4$.	Ratio of Na_2SO_4 to $MgSO_4$.
A. 18·5°	21·6	45·7	1:2·1
B. 24·5°	34·3	46·8	1:1·4

[1] See Findlay, *The Phase Rule*, 1906, p. 268.

Digitized by Google

The figures under Na_2SO_4 and $MgSO_4$ represent the number of molecules of the salt dissolved in a thousand molecules of water.

The transition point of astrakanite is about 22° C.: above this temperature the double salt exists; below it, the components are stable as independent salts. Let us examine what happens at the temperature 24·5°, which lies above the astrakanite transition temperature. At this temperature, as the figures above show, water will take up a greater number of molecules of magnesium sulphate than of sodium sulphate. But in solution these two salts will combine to form astrakanite which is less soluble and will consequently crystallise out just as the racemate did in the case of the rubidium salts. And since astrakanite contains magnesium and sodium sulphates in equimolecular proportions, it follows that at the end of the process there will be an excess of sodium sulphate left as a solid phase, along with the other solid phase astrakanite. If the vapour phase be excluded, three phases are present (solid astrakanite, solid sodium sulphate and the solution) and consequently the system is univariant and at a given temperature the solution will have a definite composition.

If astrakanite and sodium sulphate in excess be placed in contact with water at a given temperature and the mixture be agitated until equilibrium is attained, the following results are obtained for the number of molecules of magnesium and sodium sulphates dissolved in a thousand molecules of water :—

II. Solid Phases: Astrakanite and Sodium Sulphate.

Temperature.	Na_2SO_4.	$MgSO_4$.	Ratio of Na_2SO_4 to $MgSO_4$.
C. 22°	29·5	47·0	1 : 1·59
D. 24·5°	34·5	36·2	1 : 1·04
E. 30°	45·8	29·1	1 : 0·63

Repeating the process, but using in this case astrakanite and magnesium sulphate, the following results are observed :—

III. Solid Phases: Astrakanite and Magnesium Sulphate.

Temperature.	Na_2SO_4.	$MgSO_4$.	Ratio of Na_2SO_4 to $MgSO_4$.
C. 22°	28·5	46·3	1 : 1·6
F. 18·5°	34·1	42·7	1 : 1·3
G. 24·5°	26·3	47·6	1 : 1·8
H. 30°	23·0	53·1	1 : 2·3

Digitized by Google

Now, let us fix our attention upon the temperature 24·5° C. If pure astrakanite were dissolved in water at this temperature, we should get in the first place a solution containing exactly equimolecular quantities of sodium and magnesium sulphates. But in Table II., under the temperature 24·5° C., it can be seen that equilibrium is attained not when the two salts are present in equal proportions, but when there is slightly less sodium sulphate present. Consequently, in order to reach the position of equilibrium, a solution of pure astrakanite must deposit some sodium sulphate. (The case of

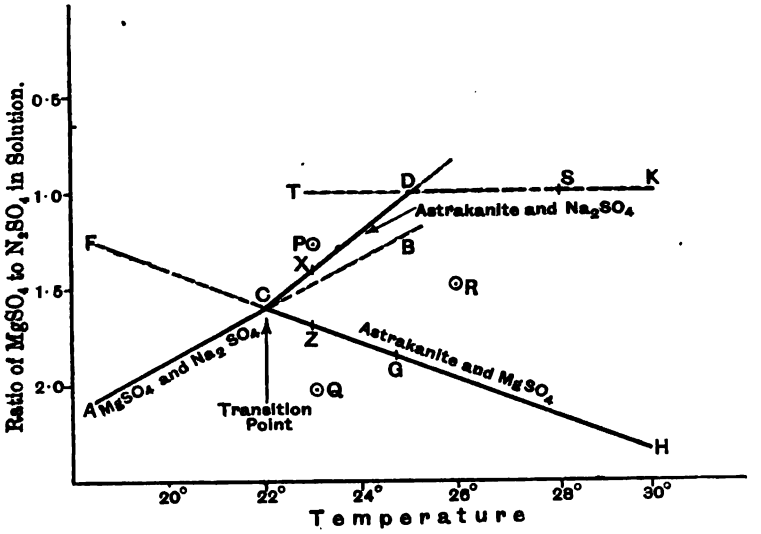


FIG. 6.

supersaturation is disregarded for the sake of convenience.) Thus it will be impossible to obtain at 24·5° C. a saturated solution of pure astrakanite.

From the data in the three tables given above a graphic representation of the relations between the various substances can be constructed. The abscissæ in Fig. 6 represent the temperatures, while the ordinates show the ratio of magnesium to sodium sulphate in the various solutions. The diagram is only a rough one.

The line ACB represents solutions saturated with magnesium and sodium sulphates, and is drawn from the data in Table I.

Digitized by Google

The line CD represents a series of solutions saturated with astrakanite and sodium sulphate, the data being taken from Table II. Similarly, the line CH is drawn from data in Table III. and represents a series of solutions in equilibrium with solid astrakanite and magnesium sulphate. If the experimental data were absolutely correct, these three lines would meet in the point C which is the transition point of the system.

An examination of the figure will show that a solution under conditions represented by the point P, will contain more sodium sulphate than a saturated solution of magnesium and sodium sulphates or of sodium sulphate and astrakanite could do. It is therefore in a state of unstable equilibrium and will begin to precipitate sodium sulphate. In other words, the line representing its change in composition will be PX, and the solution will only come into equilibrium when its composition can be represented by the point X, the temperature being kept constant throughout. Similarly, a solution represented by the point Q would contain an excess of magnesium sulphate and part of this salt would separate out until the composition of the solution became representable by the point Z. Further, a solution represented by the point R would be unsaturated with regard to both sodium sulphate and magnesium sulphate.

We are now in a position to understand what happens when pure astrakanite is dissolved in water. Take the case of a solution at 28° C. which can be represented by the point S. All solutions of pure astrakanite in water will be represented by points on the line KSD, since all such points represent solutions containing equimolecular quantities of sodium and magnesium sulphates. Now, when the temperature is lowered, the composition of the astrakanite solution will remain unchanged until the point D is reached. At that point a change must take place, for if we attempt to continue along the line DT we shall produce a solution supersaturated with regard to magnesium sulphate; hence precipitation will occur and the solution will cease to contain the two sulphates in equimolecular quantities. The point D, then, marks the lowest temperature at which astrakanite can be dissolved in water without decomposition. But the lowest temperature at which astrakanite can exist is the transition point C. The interval between these two

Digitized by Google

temperatures is called the *transition interval* for astrakanite solutions.

The occurrence of a transition interval is due to there being a difference in the solubilities of the two components of the double salt; so it is clear that the transition interval phenomenon will not be observed in the case of racemic compounds, since these are built up from dextro and lævo forms which have identical solubilities at the transition point.

5. *The Existence of Double Salts in Solution.*

From the facts described in the last section, it is obvious that when double salts are dissolved in water there is no guarantee of their existing in the solution in the double salt form; for under certain conditions they may decompose into their component materials and yield a solution which merely contains two simple salts even though the ordinary temperature limits of double salt stability are not exceeded. In order to determine whether or not the double salt exists in the solution, chemical methods are of no value and it is necessary to fall back upon purely physical properties as tests.

In certain cases, the colour of the solution gives an indication of the solute's condition. For example, when potassium chloride is added to a ferric chloride solution, the colour of the liquid changes from yellow to reddish, owing to the formation of the double salt; so that the colour-change forms a proof of double salt formation. Again, colourless lithium chloride combines with green cupric chloride to yield a garnet-coloured double salt. This criterion is, of course, of very limited applicability.

Conductivity,[1] magnetic rotation [2] and depression of freezing-point may be utilised over a wider range of substances. The values for the two separate salts are first found experimentally and their joint effect is calculated from the mixture rule. The actual value of the constants of the solution containing the supposed double salt is then determined by experiment, and if

[1] Archibald, *Trans. Nov. Scot. Inst. Sci.*, 1891, **9**, 307; Jones and his collaborators, *Amer. Chem. J.*, 1897, **19**, 83; 1899, **22**, 5; 1900, **25**, 349; Lindsay, *ibid.*, 1901, **25**, 62.

[2] Schönrock, *Zeitsch. physikal. Chem.*, 1898, **11**, 776.

Digitized by Google

this differs from the calculated value it is evident that some interaction has taken place between the salts in solution.

6. *Criteria of the Nature of Equimolecular Mixtures of Optical Antipodes.*

When equimolecular quantities of two optical antipodes crystallise from a solution together, it is obvious that one of three possible alternatives may present itself: the substances may form a true double salt; they may yield a solid solution or, finally, they may simply crystallise out as a conglomerate, a mixture of crystals of each separate antipode.

It is well known that the melting-point of a substance is lowered by the solution in it of a foreign material. For example, the melting-point of water is very considerably lowered when salt is added to the liquid. Now, the same rule will hold even if the relative amount of the solvent be decreased; and, consequently, if the amount of solute be increased and that of the solvent be diminished, a minimum value for the melting-point of the mixture will eventually be obtained. If the process be continued, it is clear that finally the solvent will be present in less quantity than the solute; so that their relative positions are altered; what was at first the solvent now becomes the solute. When this point has been passed, the melting-point of mixtures of the two bodies will rise instead of falling, for the proportion of solvent to solute is now steadily increasing.

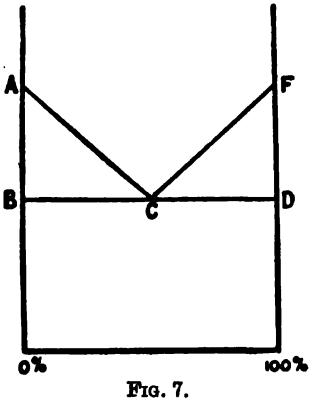


FIG. 7.

This reasoning can now be applied to the case of solid mixtures of two optical antipodes. Suppose that they do not combine with each other chemically; in that case a conglomerate or a solid solution will be present.

If in Fig. 7 BA represents the melting-point of, say, the dextro form; then as some of the lævo variety is gradually added to the pure dextro form, the melting-point of the mixture will fall until it reaches a minimum at C, when equal quantities of

Digitized by Google

the dextro and lævo forms are present in the mixture. Now let F represent the melting-point of the lævo form. Since the melting-points of optical antipodes are equal, DF will be equal to BA. As more and more of the dextro form is added to the lævo substance, the melting-point of the mixture will fall just as in the last case; and in the end it will be represented by the point C. It is evident that at C both antipodes will be present in equal proportions. Hence, if to such a mixture as this a small quantity of either antipode be added, the melting-point of the new mixture will be *higher* than that of the equimolecular mixture.

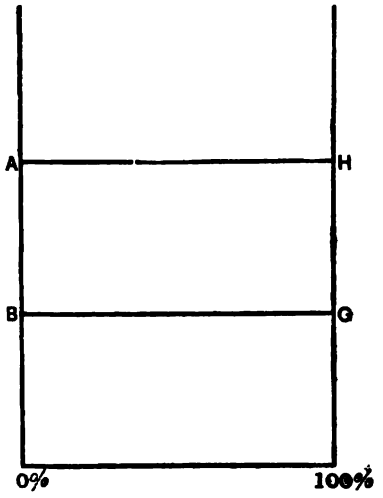


FIG. 8.

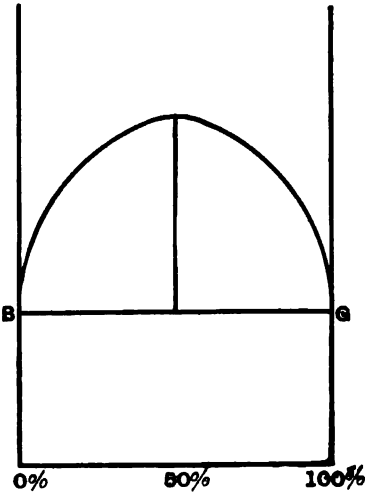


FIG. 9.

In the case of a mixed crystal composed of two optical antipodes, there are various possible forms for the curve representing the melting-points of a set of mixtures of different composition. Of these possible curves, only two have been as yet observed in practice. They are of the forms shown in Figs. 8 and 9.

It has been found that the two camphor oximes,[1] for instance, form a series of mixed crystals, all of which have the same melting-point. The curve of the melting-points of these mixtures is therefore a straight line. An example of the other

[1] Findlay, *Phase Rule*, 1906, p. 187.

Digitized by Google

form of curve is furnished by the carvoximes.[1] In this case, a maximum is found, as shown in the figure.

With regard to racemic substances, in their case an actual compound is present. Consequently, since there are three substances in the system (the two antipodes and the racemic compound), there will be two sets of curves, one showing the relations between the dextro antipode and the racemic substance, the other illustrating these between the racemic compound and the lævo isomer. Figs. 10 and 11 show possible forms of the curves.

This case is really a repetition of the first one dealt with above, but here the figure is repeated twice over. If the racemic compound be considered as taking the place of one of

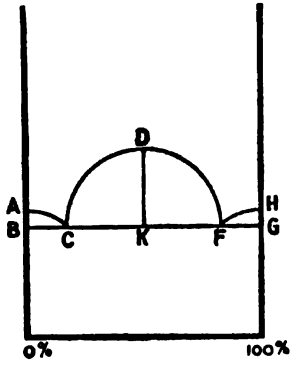


Fig. 10.

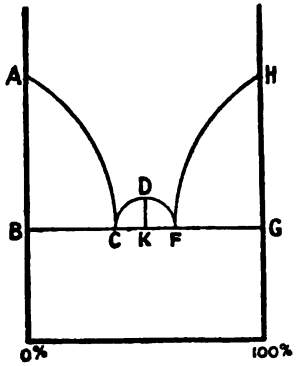


Fig. 11.

the antipodes; A represents the melting-point of the dextro form, H that of the lævo isomer, and D that of the racemate. The abscissæ along BK represent graphically the percentages of dextro isomer and racemic compound present; while those along KG represent the percentages of racemate and lævo antipode. It can be seen that an addition of either dextro or laevo form to the racemate will result in a lowering of the melting-point.

We are now in a position to understand the method to be applied. We have before us an optically inactive crystalline body which is made up of equal quantities of dextro and lævo forms. In order to decide whether it is a conglomerate, a mixed crystal or a racemate its melting-point must first be

[1] Adriani, *Zeitsch. physikal. Chem.*, 1900, **33**, 469.

Digitized by Google

taken. A small quantity of one of the antipodes is then added to the inactive material and the melting-point of the mixture is determined. This process is continued; each time rather more of the antipode being added. In this way it is possible to plot the curve of the melting-points of the mixtures. If this curve is of the type shown in Figs. 8 or 9, then the original material was a solid solution. If, on the other hand, the curve shows first a fall in the melting-point and then a rise as the quantity of antipode in our mixture is increased, it is obvious that a true racemic compound is present; for the curve will resemble one of those shown in Figs. 10 and 11.

Finally, if the addition of more and more antipode to the inactive body produces a series of mixtures whose melting-points are higher and higher, then the material is evidently merely a conglomerate; and the curve will be one of the branches of that shown in Fig. 7.

Digitized by Google

CHAPTER IV.

THE PROBLEM OF THE OCEANIC SALT DEPOSITS.

1. *The Stassfurt Salts.*

In various parts of the earth, large tracts of sedimentary deposits have been discovered which contain high percentages of common salt. Such strata form the most valuable source of salt at the present day; but in addition to their practical value they have a further claim to attention on account of some physico-chemical questions which their existence suggests. The most important deposit is to be found at Stassfurt, and its characteristics may be described briefly before these problems are discussed.

The salt strata in the Stassfurt district may be divided into four types. Beginning at the top, there is a layer of carnallite ($MgCl_2 . KCl . 6H_2O$) mixed with a little rock salt; this bed may be anything up to 30 metres in depth. Below this comes a stratum of rather greater thickness made up of kieserite ($MgSO_4 . H_2O$); the percentage of rock salt in this layer is rather greater than in the carnallite bed. Deeper still lies a zone in which the prevailing mineral is polyhalite ($MgSO_4 . K_2SO_4 . 2CaSO_4 . 2H_2O$); while the fourth stratum is chiefly made up of anhydrite ($CaSO_4$). The polyhalite and anhydrite regions are remarkable for the manner in which the characteristic minerals are interspersed with regular layers of rock salt: first comes a layer of rock salt then a layer of polyhalite, then another layer of rock salt and again a layer of polyhalite. Below the anhydrite strata lies the main bulk of the common salt deposits. Fig. 12 shows an ideal section of these strata.

While the problem of the conditions under which the Stassfurt beds were laid down is most interesting from the point of view of geology, it is evident that very little progress

Digitized by Google

could be made towards its solution by purely geological methods. Apart from the suggestion that the alternating layers of salt and polyhalite, etc., owed their origin to the change of temperature with the seasons, there seemed little chance of any results of value being obtained. In the hands of van't Hoff and his collaborators, however, the whole question has been opened up and developed to such a point that even the temperature of the period at which any particular series of beds

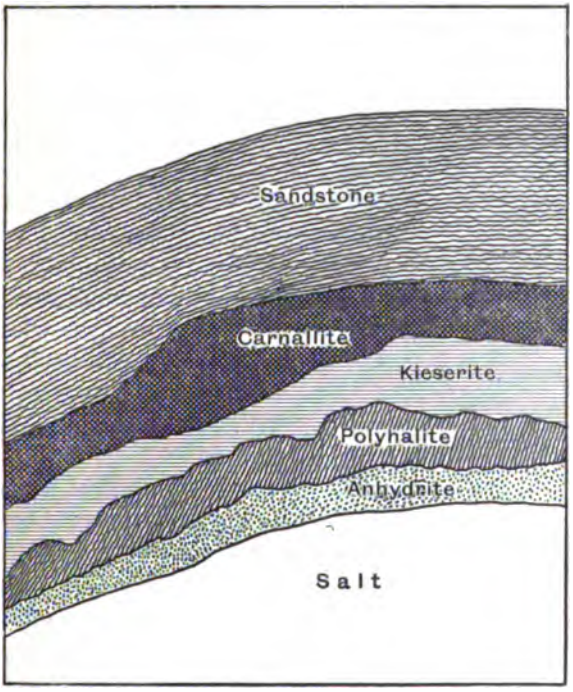


FIG. 12.

was deposited can be determined with moderate accuracy. In the following pages a brief account of these researches will be given.

2. *The Researches of Usiglio and van't Hoff.*

From the composition of the Stassfurt deposits, it seems probable that they were originally formed by the evaporation of sea-water: and hence it may at first sight appear perfectly simple to repeat the process in the laboratory by evaporating

Digitized by Google

sea-water to dryness. This was carried out on a large scale by Usiglio[1]; but the results obtained by him failed to correspond with the natural deposits in several important respects. For example, he obtained neither kieserite, polyhalite nor anhydrite, though these substances are the predominant factors in the middle strata at Stassfurt.

Several causes probably contributed to the failure of Usiglio's experiments. In the first place, at the time when he carried out his work the question of transition temperatures had not been thoroughly investigated; and consequently this important factor was perforce left out of the calculation. This alone would have made success very doubtful in the case of the deposition of double salts, but there were many other drawbacks to his method. In artificial experiments, even on the largest scale, there are many sources of error which prevent the action from proceeding on lines exactly parallel to those followed by the natural process. In a small tank there may be supersaturation; the layers of two deposits may be so intimately mixed that it is difficult to determine which came down first; or, again, after one solute has separated out from the solution its crystals may become crusted over with layers of a second solute, so that there may be no solid phase of the first solute in contact with the solution.

It is therefore evident that in order to obtain an insight into the conditions under which the Stassfurt strata were laid down, more refined methods must be employed than mere evaporation of sea-water. The question remained practically at this stage until the year 1887, when van't Hoff[2] and his collaborators attacked the problem from a different point of view.

Instead of taking a solution like sea-water, which contains a very large series of solutes, van't Hoff in his researches worked always from simple to more complex cases. The simplest case is, of course, that in which there is only a single solvent and a single solute. In such a system, evaporation would proceed until the solvent was saturated with the solute: after which, if more solvent evaporated, the solute would begin

[1] Usiglio, *Ann. Chim. Phys.*, (3), 1849, **27**, 92, 172.

[2] van't Hoff, *Zur. Bildung der ozeanischen Salzablagerung*, Vol. I., 1905; Vol. II., 1909.

Digitized by Google

to separate out from the mother liquor. The case of two or more solutes is more complicated, and must be dealt with in the next section.

3. *Solutions of Potassium and Sodium Chlorides.*

If two salts such as sodium chloride and magnesium sulphate be dissolved in water, it is evident that a double decomposition will at once take place; so that if the solution were evaporated, a mixture of magnesium sulphate, magnesium chloride, sodium chloride and sodium sulphate would be obtained. The original two salts would give rise to two new salts, thus complicating the problem considerably. It becomes clear, therefore, that in order to deal with a case which does not involve these complications the problem must be restricted to two salts having a common ion, such as two chlorides or two potassium salts. Further, two salts must be chosen which do not combine together to yield a double compound, as this would confuse the matter to some extent.

As a concrete example the case of potassium chloride and sodium chloride may be selected, and 25° may be fixed as the temperature at the time of the experiment. Under these conditions, a saturated solution of sodium chloride contains 111 molecules of salt in 1000 molecules of water. Under the same conditions, a saturated solution of potassium chloride contains 88 molecules of salt in 1000 molecules of water.

Now, suppose that to a saturated solution of sodium chloride some potassium chloride be added, two results will follow. In the first place, potassium chloride will be dissolved; but as more and more is added it will finally be present in greater quantity than the solution can take up, and further addition of it will have no effect. The solution thus obtained is saturated with respect both to potassium chloride and to sodium chloride. It is termed a *constant solution*, and is composed of

Potassium chloride	89 molecules
Sodium chloride	89 ,,
Water	1000 ,,

These relations must now be expressed graphically (see Fig. 13).

Digitized by Google

Take two rectangular axes OX and OY and let distances measured along OY represent the number of molecules of potassium chloride in 1000 molecules of water, while distances along OX represent the analogous measurements for sodium chloride. Then P will indicate the saturation point of the solution with regard to potassium chloride, since OP is 88 units in length. Further, R represents the saturation point of a solution of sodium chloride in water, OR being 111 units in length. The co-ordinates of the point Q are, of course, 39 along OY and 89 along OX.

A consideration of the figure will show that the composition of any possible solution of sodium chloride and potassium chloride can be represented by some point inside the figure OPQR. Further, points outside OPQR represent merely ideal

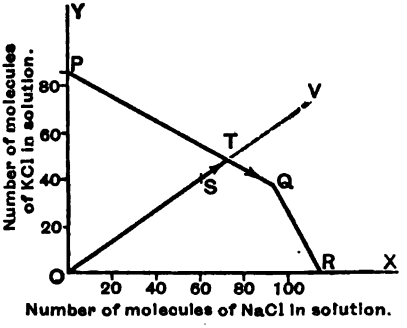


FIG. 18.

solutions; for in practice any attempt to add to the solution more salt than can be represented by a point within the figure would result merely in the deposition of a corresponding amount of salt.

Consider next the case of some definite solution, and see if its behaviour on evaporation can be foretold. Take as an example a solution containing 40 molecules of potassium chloride and 60 of sodium chloride in 1000 molecules of water. To obtain the point corresponding to this composition, it is necessary to measure 40 units along OY and 60 units along OX, and in this way the point S is found. When this solution is evaporated, it is evident that at first the ratio of potassium to sodium chloride contained in it remains unaltered; for only water is removed from the system. The solution

Digitized by Google

therefore becomes more concentrated, while at the same time the ordinate and the abscissa of the point representing it maintain the same ratio to each other as before. Now the ordinate of any point on OSV is obviously two-thirds of the corresponding abscissa; and the line OS represents a series of solutions in which the ratio of sodium to potassium chloride remains always the same, though the proportion of water present decreases as the distance from O increases.

As the solution is steadily evaporated then, the point representing its composition will move from S along OSV away from O. When it reaches the line PQ it represents a solution which is saturated with potassium chloride; and consequently some of that salt will separate out. If the evaporation be continued it is obvious that the point representing the solution's composition cannot move along the dotted line TV, as no such solution can exist; experiment shows that it moves as indicated by the arrow, in the direction of Q. When, by further evaporation, the composition of the solution becomes that which is represented by the point Q, no further change takes place; the two solutes are then present in such proportions that their rates of crystallisation are exactly proportional to the quantity of each substance which is present in solution. The solution therefore yields crystals of a constant composition and goes down to dryness without change in concentration. The point Q is termed the *end-point of crystallisation.*

These results van't Hoff[1] summarises in the following rule: "A solution in depositing a solute changes its composition *away from* that of a saturated solution of this solute alone".

4. *The Case of Carnallite.*

In the foregoing section we examined the case of a solution containing two non-combining solutes: in the present section a slightly more complicated case comes under consideration. When solutions of magnesium and potassium chlorides, under certain conditions of temperature, are mixed, a double salt called carnallite is formed, which has the composition—

$$MgCl_2 . KCl . 6H_2O$$

It is evident that the formation of this body differentiates the

[1] van't Hoff, *Zur Bildung der oceanischen Salzablagerung*, I., 12.

Digitized by Google

case of a solution of magnesium and potassium chlorides from that of the solution of sodium and potassium chlorides which was described in the last section. Instead of two solutes there are now three: magnesium chloride, potassium chloride and carnallite. Thus it is necessary to determine the solubility relations of—

1. Potassium chloride in water.
2. Magnesium chloride in water.
3. Carnallite in magnesium chloride solution.
4. Carnallite in potassium chloride solution.

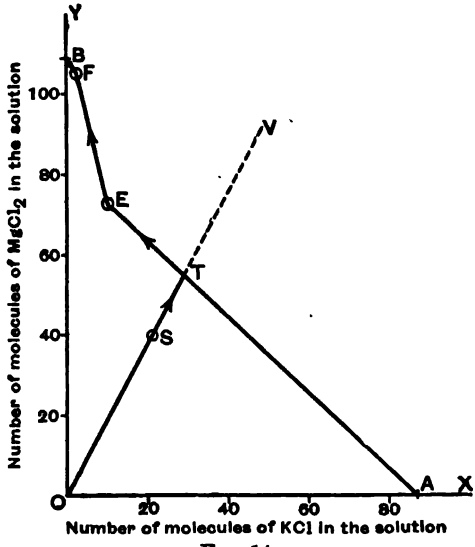


FIG. 14.

As in the last case, two rectangular axes are used, along one of which the number of molecules of potassium chloride in 1000 molecules of water is measured, while along the other the number of molecules of magnesium chloride in the same quantity of water is marked off. The point A (see Fig. 14) represents a saturated solution of potassium chloride (88 KCl in 1000 molecules H_2O). The point B represents a saturated solution of magnesium chloride (108 molecules $MgCl_2$ in 1000 H_2O).

Now, to the saturated potassium chloride solution represented by the point A, add some magnesium chloride. The two salts at once combine to form carnallite Consequently the

Digitized by Google

solution is really one containing carnallite and potassium chloride; so that by the continual addition of magnesium chloride we are really approaching a constant solution of carnallite and potassium chloride instead of a constant solution of magnesium and potassium chlorides. This constant solution is obtained when these are present:—

Potassium chloride	11 molecules.
Magnesium „	72·5 „
Water	1000 „

This point is represented on the figure by the point E.

If we begin with a saturated solution of magnesium chloride and add to it potassium chloride, a similar process takes place. The added potassium chloride combines with the excess of magnesium chloride, forming carnallite again: but in this case the constant solution formed by continued addition of potassium chloride is one containing carnallite and magnesium chloride and having the composition:—

Potassium chloride	2 molecules.
Magnesium „	105 „
Water	1000 „

In the figure this is represented by the point F.

If, as in the previous section, we take the case of a solution of the composition shown by the point S, we can now tell exactly what will happen when it is evaporated. In the first place, water will be driven off and the point S will move along OV towards V until it reaches T, beyond which it cannot go. At this point there is an excess of potassium chloride in the solution, and as the concentration goes on it is found that this separates out. That is to say, the point representing the solution will move from T along TE towards E.

At this point there are two possible courses open. If we remove from the vessel all the solid potassium chloride which separates out from the solution, the composition of the solution will follow the line EF, becoming richer in magnesium chloride. In this case F is the end-point of crystallisation. On the other hand, if we do not remove the solid potassium chloride from the solution, it is attacked by the magnesium chloride with the formation of carnallite which then crystallises out. In this case the composition of the solution remains constant, and a continuous separation of carnallite takes place.

Digitized by Google

Of course in this, as well as in the previous figure, the lines should not be quite straight, but the deviation for straightness is probably not great.

5. *The Case of the Chlorides and Sulphates of Magnesium and Potassium.*

It is now necessary to examine a still more complicated case, in which the number of possible constant solutions increases greatly. If to a solution of potassium chloride some magnesium sulphate be added, owing to the consequent double decomposition, a solution is formed which contains four salts: potassium chloride, potassium sulphate, magnesium chloride and magnesium sulphate. It will be seen later that other salts come into existence as well, but for the present we may confine our attention to these four.

As in the last case, it is first necessary to determine the solubility of each of the four salts in water. The number of molecules of each salt which can be dissolved in 1000 molecules of water is given in the following table:—[1]

A. K_2Cl_2	44 molecules.*
B. $MgCl_2$	108	,,
C. $MgSO_4.7H_2O$	55	,,
D. K_2SO_4	12	,,

To this table a second must be added showing the relations between carnallite and its components:—

	Molecules of K_2Cl_2.	Molecules of $MgCl_2$ saturate 1000 H_2O.
E. K_2Cl_2 and carnallite	5·5	72·5
F. $MgCl_2$,, ,,	1	105

Then the relations of magnesium chloride to the two hydrates of magnesium sulphate must be taken into account as well as the reciprocal relations of the two latter bodies. These are expressed in the following figures:—

	Molecules of $MgCl_2$.	Molecules of $MgSO_4$ saturate 1000 H_2O.
G. $MgCl_2$ and $MgSO_4.6H_2O$	104	14
H. $MgSO_4.7H_2O$ and $MgSO_4.6H_2O$	73	15

[1] For these and the following figures and diagrams, van't Hoff's *Oceanischen Salzablagerungen* has been utilised.

* van't Hoff reckons potassium chloride in terms of double molecules in order to bring it into line with the other salts.

Digitized by Google

The formation of $MgSO_4 . 6H_2O$ is due to the dehydrating action of the magnesium chloride, so that the hexahydrate is formed only in solutions containing that substance.

When the sulphates of magnesium and potassium occur in the same solution, there is a possibility of the formation of the double salt schönite, $MgSO_4 . K_2SO_4 . 6H_2O$; so that this in turn must be taken into account. Two more sets of data are therefore obtained: one showing the relation of magnesium sulphate to schönite, the other giving the relation of schönite to potassium sulphate:—

	Molecules of $MgSO_4$.	K_2SO_4 in 1000 molecules H_2O.
J. $MgSO_4 . 7H_2O$ and schönite . .	58·5	5·5
K. K_2SO_4 and schönite . . .	22	16

To complete the series, it is necessary to know the relations between potassium sulphate and potassium chloride. These are given in the following figures:—

	Molecules of K_2Cl_2.	K_2SO_4 in 1000 molecules H_2O.
L. K_2SO_4 and K_2Cl_2 . . .	42	1·5

In the foregoing data each substance has been taken separately; then their double salts have been dealt with; and finally they have been taken in pairs. The next step is to take the figures found when the substances are present three at a time. These data are given in the table below:—

	Molecules of K_2Cl_2.	$MgCl_2$.	$MgSO_4$ in 1000 molecules H_2O.
M. K_2Cl_2, K_2SO_4, schönite . . .	25	21	11
N. K_2Cl_2, $MgSO_4 . 7H_2O$, schönite .	9	55	16
P. K_2Cl_2, $MgSO_4 . 7H_2O$, $MgSO_4 . 6H_2O$	8	62	15
Q. K_2Cl_2, carnallite, $MgSO_4 . 6H_2O$.	4·5	70	13·5
R. $MgCl_2$, carnallite, $MgSO_4 . 6H_2O$.	2	99	12

These figures complete the data required, and they must now be expressed graphically. For this purpose van't Hoff chose rectangular axes as in the previous cases, and carried out the construction of his figure in the following manner (see Fig. 15): Along the axis OA he measured off 44 units, corresponding to the quantity of potassium chloride required to saturate a solution. Similarly, the point B represents the saturation point of a solution of magnesium chloride; point C

Digitized by Google

represents a saturated solution of magnesium sulphate; and D a solution saturated with potassium sulphate. The positions corresponding to the constant solutions are then filled in as before at E, F, G, H, K and L.

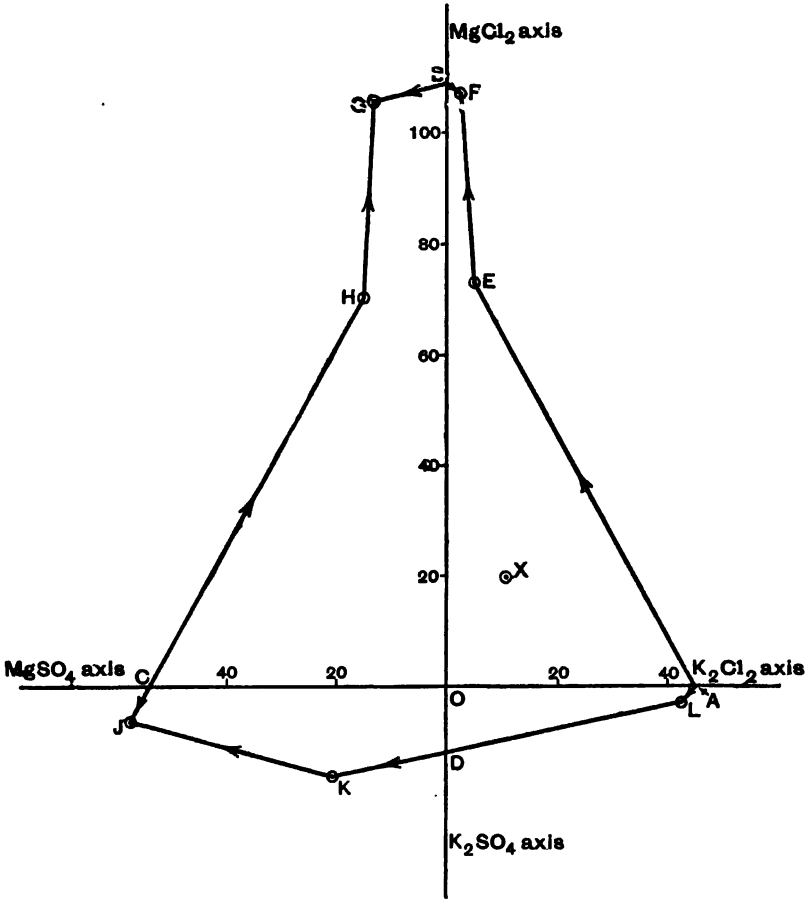


FIG. 15.

The diagram thus obtained is not satisfactory, however, as the following consideration shows:—

Take the concrete case of two solutions, one of which (I.) contains—

10	molecules	K_2Cl_2
20	,,	$MgCl_2$
0	,,	$MgSO_4$

Digitized by Google

while the other (II.) contains—

30 molecules K_2Cl_2
20 „ $MgCl_2$
20 „ $MgSO_4$

If an attempt is made to insert these in the plane figure (Fig. 15), we must for case (I.) measure from O, 10 units along OA, then turn at right angles and measure 20 units parallel to the direction OB. This will place us at the point X which should thus represent the composition of the solution I. In the case of solution (II.), we start again from O; measure 30 units towards A to represent the quantity of K_2Cl_2 present; then in the reverse direction—towards C—measure 20 units to represent the amount of $MgSO_4$ in the solution. This leaves us at a point 10 units from O in the direction OA. We then measure from this point 20 units up the paper in the direction OB, and this brings us in this case also to the point X. Thus two solutions would be represented by the same point X.

In order to avoid such confusion, van't Hoff inserted another co-ordinate into his scheme. From every point in the plane of the paper he raises a perpendicular whose length is proportional to the number of molecules of all kinds which are present in the solution. For example, in the two cases given above a perpendicular would be raised from the point X; on this perpendicular we should cut off a distance of 30 units (10 molecules K_2Cl_2 + 20 molecules $MgCl_2$ = 30 molecules in all) and the point thus obtained would represent solution (I.). Since solution (II.) contains 70 molecules we should have to travel 70 units up the perpendicular from X before we arrived at the point which represents its composition.

When in this way the five points corresponding to the solutions, M, N, P, Q and R, have been filled in, the outline of a space model is produced whose appearance is shown in the perspective sketch (Fig. 16). Each face of this model represents a solution saturated with the salt whose name is placed upon it in the figure.

A few words will make clear how this model can be utilised. As far as the edges are concerned, there is no difficulty: the lines AE, BF, etc., have exactly the same meaning as the lines in Figs. 14 and 15; and the route followed in crystallisation

Digitized by Google

can be foretold by the van't Hoff Rule just as in the previous cases. The arrows in the figure indicate this.

The case is not much more complicated if we start from a solution whose composition is represented by a point on one of the faces. Suppose we take the point S in Fig. 16. This

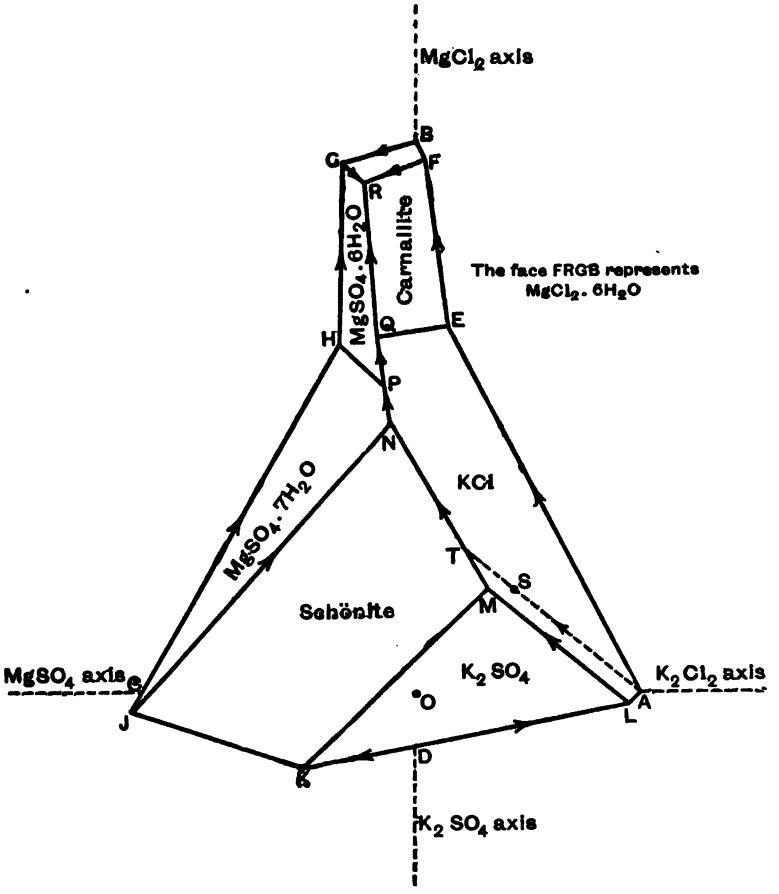


FIG. 16.

point lies on the potassium chloride face so that an evaporation of the solution will cause the separation of that salt. Since the point A represents a saturated solution of potassium chloride, we join S to A. Then, according to the van't Hoff Rule, the point representing the composition of the solution

Digitized by Google

will pass (as the solution is evaporated) along AS produced, away from A. It will thus cut the edge MN in T, and thereafter the crystallisation process will follow the direction of the arrows as shown.

It is unnecessary to enter in detail into cases in which the point representing the composition of the original solution lies inside the surface of the space model; it is, of course, more complicated, but the same rule applies there also.

Since the space model is somewhat clumsy, it may be

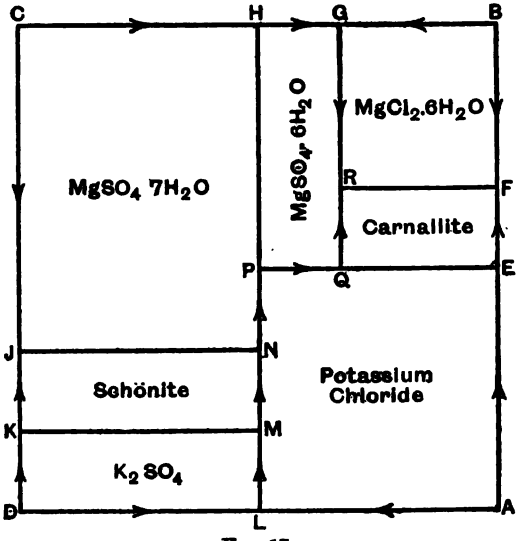


FIG. 17.

replaced in a way by a simplified figure which gives equally well the relations between the various faces. (See Fig. 17.)

6. *The Case of Five Salts.*

If to the salts dealt with in the last section sodium chloride be added, a solution is obtained which closely corresponds to that from which the upper bed of the Stassfurt must have been laid down. The case is an extremely complicated one, there being no fewer than twenty-six different possible solutions and combinations of solutes to be taken into account. It will be sufficient to reproduce van't Hoff's sketch of the space model (Fig. 18) as well as the plane arrangement corresponding to it

Digitized by Google

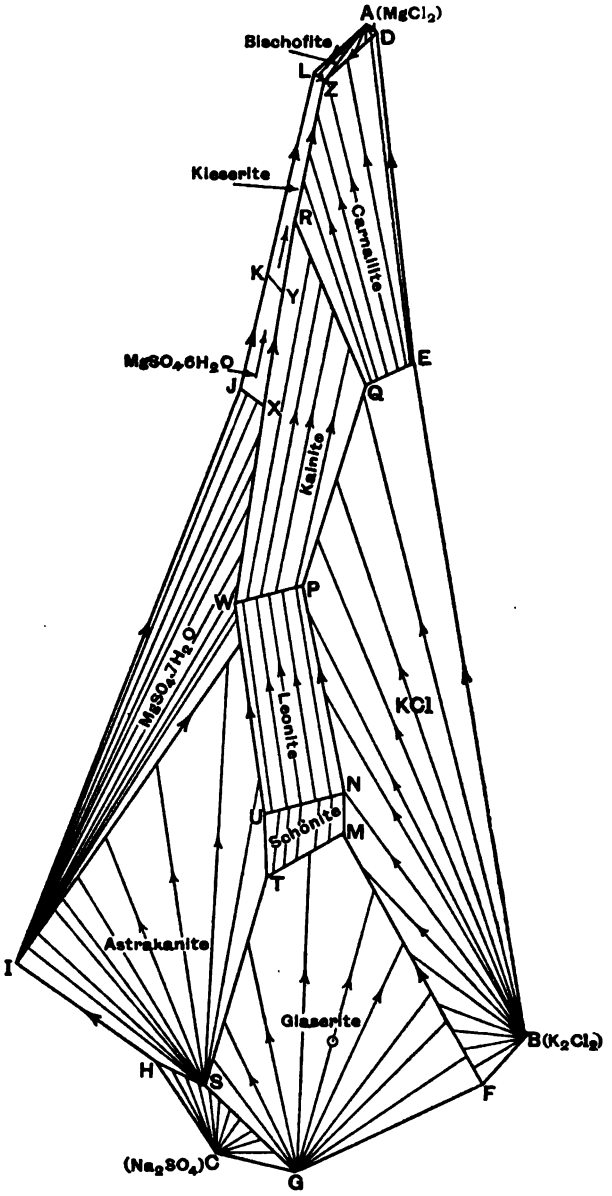


FIG. 18.

Digitized by Google

(Fig. 19). This model corresponds to a set of experiments carried out at a temperature of 25° C.

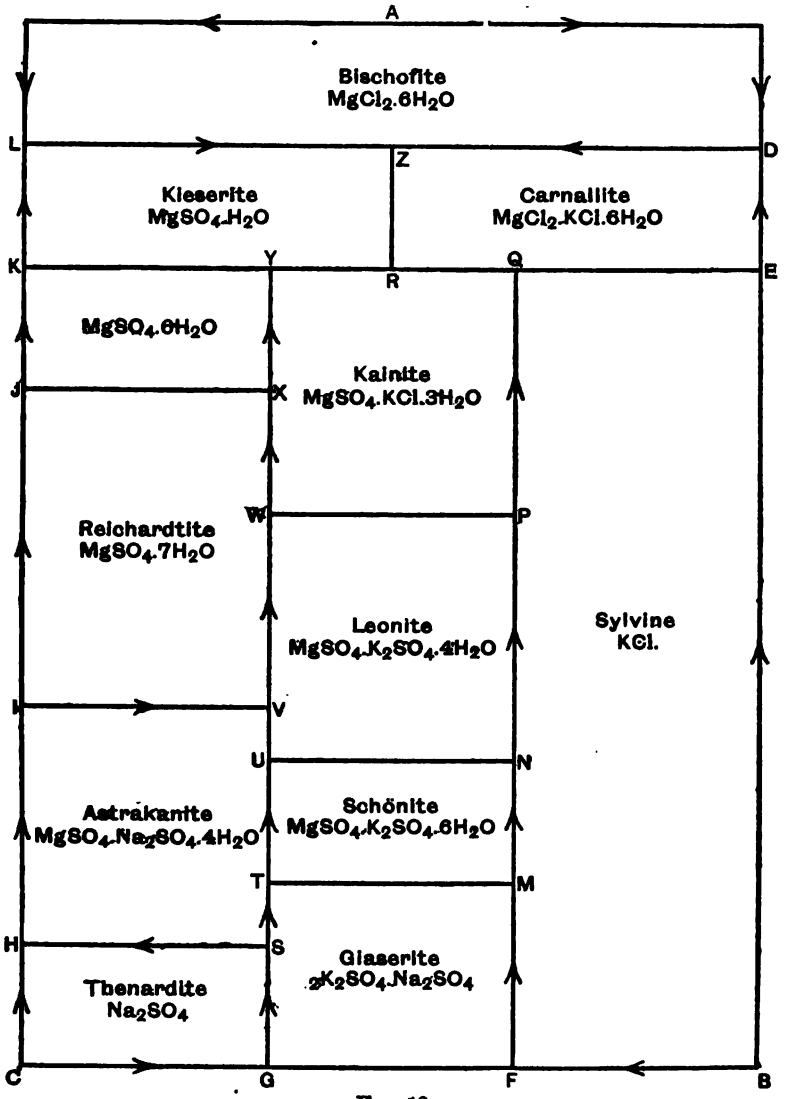


FIG. 19.

7. *The Influence of Time.*

At this point it is necessary to deal with another factor in the question which complicates matters considerably. In the

Digitized by Google

course of his earlier researches, van't Hoff found that in many of the solutions employed by him supersaturation occurred, with the result that salts which should theoretically have appeared at a certain stage of the evaporation process did not begin to crystallise from the solution until much later. The salts which thus appeared in the wrong place were kieserite ($MgSO_4 . H_2O$), leonite ($MgK_2(SO_4)_2 4H_2O$) and kainite ($MgSO_4 . KCl . 3H_2O$). Van't Hoff, in order to detect the presence of these bodies, brought into action the differential tensimeter. The salts which now and then fail to crystallise at the points where they are expected are all dehydration products of salts already present in solution: they must therefore be formed in a solution whose tension is smaller than that of the water of crystallisation in the undehydrated salts. By means of the differential tensimeter it is possible to determine which form will appear.

For example, at 25° C., the tension of the water of crystallisation of magnesium sulphate hexahydrate is greater than the tension of a solution containing magnesium sulphate hexahydrate, carnallite and magnesium chloride: and it is therefore to be expected that when the hexahydrate is brought into contact with the solution, it will be dehydrated. This actually occurs in practice. Again, at 25° C., a saturated solution of schönite may be supersaturated with leonite, which contains two molecules less water of crystallisation: so that this salt must be taken into account when the examination of the solution is made.

These supersaturation questions naturally complicate the problem very much; for they result in crystallisations hanging fire to a greater or less extent, and thus creating a discrepancy between theory and practice.

There appears to be some relation between the retardation of crystallisation and a number which is called the *mean valency* of compounds. This mean valency is obtained in the following manner: As a numerator we take the sum of the number of valencies of the ions into which the salt dissociates in solution and add four units for each molecule of water of crystallisation. The denominator of the fraction is obtained by adding together the number of ions and three units for each molecule of water of crystallisation. A few examples will make the matter clearer:—

Digitized by Google

Gypsum . .	$CaSO_4 . 2H_2O$.	$\frac{2+2+8}{1+1+6} = 1{\cdot}5.$
Glauberite . .	$CaNa_2(SO_4)_2$ . .	$\frac{2+2+4}{1+2+2} = 1{\cdot}6.$
Colemanite . .	$Ca_2B_6O_{11} . 5H_2O$.	$\frac{4+18+20}{2+6+15} = 1{\cdot}83.$
Ascherite . .	$MgBO_2H$ . .	$\frac{2+3+1}{1+1+1} = 2{\cdot}0.$

In this series of substances there will be greater retardation in the crystallisation of gypsum than in that of glauberite, while ascherite will show the greatest resistance to crystal formation.

8. *Paragenesis and the Influence of Temperature.*

An examination of Fig. 19 will show that some of the rectangles are conterminous, while others do not touch each other. For example, the rectangles representing kainite and schönite do not touch each other in any point; while the rectangle denoting sylvine touches those symbolising kainite, leonite, schönite and glaserite. This indicates, as has been shown experimentally to be the case, that while sylvine can co-exist in solution with kainite at 25° C., astrakanite cannot do so. But if two substances cannot co-exist in solution it is evident that they cannot occur together in the same salt stratum; for their simultaneous occurrence would show that they had crystallised out side by side from the solution. Hence the space model can be made to serve another purpose, *viz.*, to indicate whether or not we can expect to find two minerals occurring in the same geological layer. Further, if astrakanite and kainite occur in the same stratum, then we can at once say that the temperature at the time of deposition could not have been 25° C.

This question of *paragenesis*, as van't Hoff called it, led him to take up an elaborate series of supplementary researches, in the course of which he determined in the presence of sodium chloride the transition temperatures of all the double salts involved in the Stassfurt problem. The results are given in the following table:—

Digitized by Google

Mineral.	Composition.	Existence limits.	
		Upper.	Lower.
Thenardite . . .	Na_2SO_4	—	18·5°
Glauber's salt . . .	$Na_2SO_4 . 10H_2O$ . . .	18°	—
Kieserite	$MgSO_4 . H_2O$ . . .	—	18·0°
Schönite	$MgSO_4 . K_2SO_4 . 6H_2O$ . .	26°	—
Reichardtite . . .	$MgSO_4 . 7H_2O$ . . .	31°	—
Hexahydrate . . .	$MgSO_4 . 6H_2O$ . . .	35·5°	18°
Langbeinite . . .	$K_2SO_4 . 2MgSO_4$ . . .	—	37°
Loewite	$2MgSO_4 . 2Na_2SO_4 . 5H_2O$.	—	43°
Vanthoffite . . .	$MgSO_4 . 3Na_2SO_4 . 4H_2O$.	—	46°
Astrakanite . . .	$MgSO_4 . Na_2SO_4 . 4H_2O$.	60°	4·5°
Leonite	$MgSO_4 . K_2SO_4 . 4H_2O$ . .	61·5°	18°
Kainite	$MgSO_4 . KCl . 3H_2O$ . .	83·0°	—

These data furnish the means of foretelling the outlines of the crystallisation process which will take place when a solution containing these salts is evaporated. Take the temperature 84° C. as a starting point. At that temperature, the only double salts which can exist are carnallite, langbeinite, glaserite, vanthoffite and loewite; but crystals of bischofite ($MgCl_2$), kieserite ($MgSO_4 . H_2O$), thenardite (Na_2SO_4) and sylvine (KCl) may also be formed.

When the liquid cools down one degree, kainite ($MgSO_4 . KCl . 3H_2O$) makes its appearance, as we have then reached its upper existence limit, 83° C. The solution will go on depositing these ten minerals until the temperature falls to 61·5° C., at which point leonite ($MgSO_4 . K_2SO_4 . 4H_2O$) first occurs. One and a half degrees lower, astrakanite ($MgSO_4 . Na_2SO_4 . 4H_2O$) begins to be formed. The temperature must now fall to 46° C. before further change takes place; but at this point we reach the lower limit for the existence of vanthoffite ($MgSO_4 . 3Na_2SO_4 . 4H_2O$), and it consequently ceases to be deposited from the solution. After the temperature reaches 43° C., loewite ($2MgSO_4 . 2Na_2SO_4 . 5H_2O$) in turn disappears; and at 37° C. langbeinite ($K_2SO_4 . 2MgSO_4$) also ceases to crystallise out. At 35·5° C. it becomes possible for the hexahydrate of magnesium sulphate to be deposited; at 31° C. the heptahydrate reichardtite appears, and at 26° C. we begin to find deposits of schönite ($MgSO_4 . K_2SO_4 . 6H_2O$).

When the temperature reaches 18° C., three simultaneous

Digitized by Google

changes occur; for on the one hand we reach the upper limit of existence of Glauber's salt, which therefore makes its

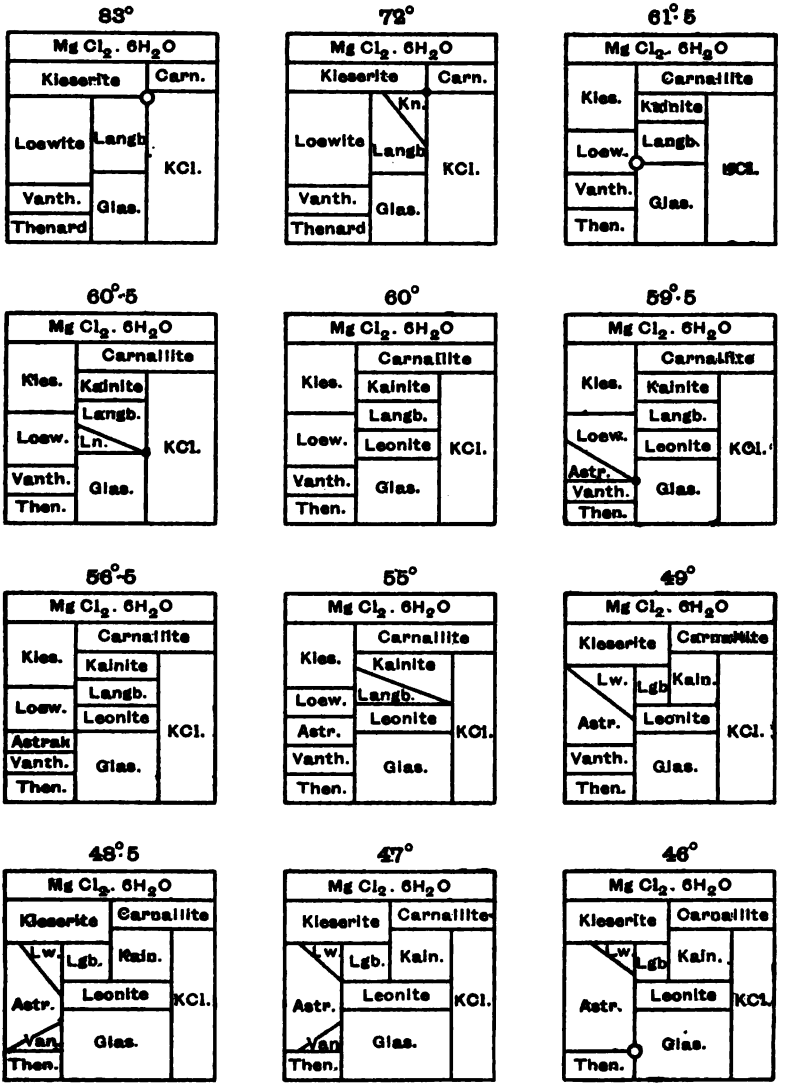


FIG. 20.

appearance; while on the other hand we find that both kieserite ($MgSO_4 . H_2O$) and leonite ($MgSO_4 . K_2SO_4 . 4H_2O$) disappear at this point.

Digitized by Google

At 13·5° C. thenardite (Na_2SO_4) disappears, Glauber's salt taking its place. Then, if the temperature falls half a degree,

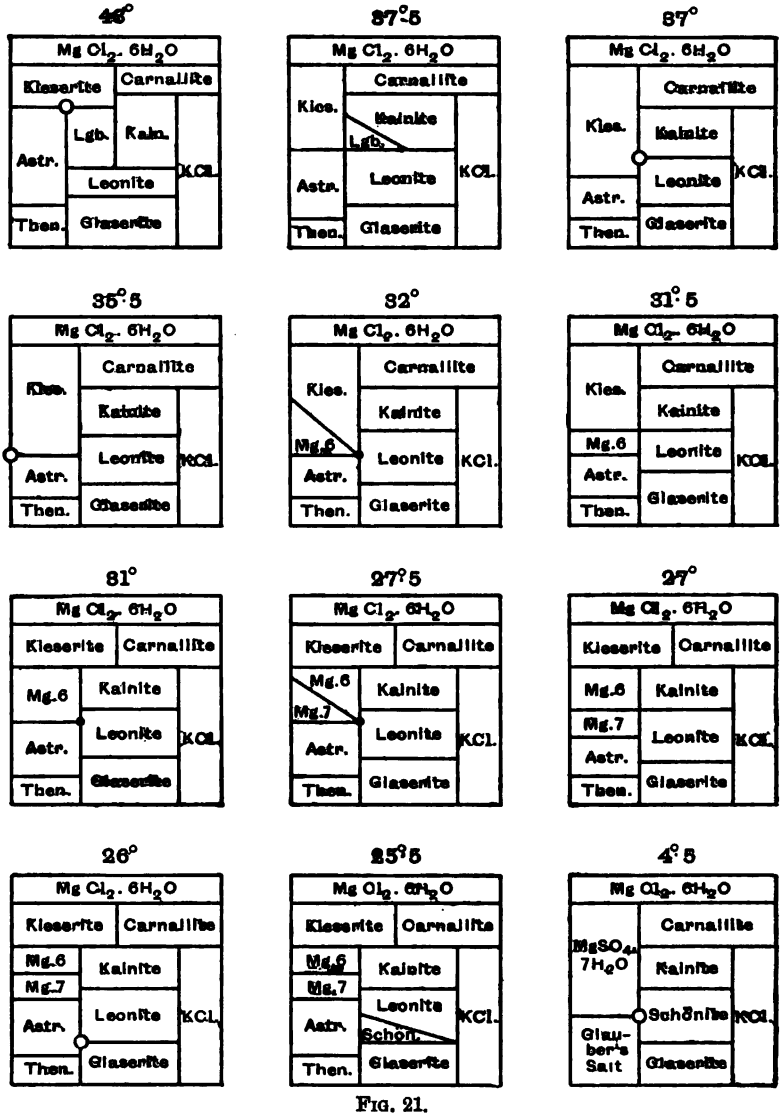


FIG. 21.

we reach the lower limit of existence of the hexahydrate of magnesium sulphate. Finally, at 4·5° C. astrakanite ceases to exist.

Digitized by Google

	Langbeinite.	Vanthoffite.	$MgSO_4 . 6H_2O$.	Carnallite.	Leonite.	Glaserite.	KCl.	Kainite.	Kieserite.	Astrakanite.
Thenardite .	–*	above 46°	–	–	–	+†	–	–	–	to 49°
$MgSO_4 . 7H_2O$.	–	–	to 81°	–	to 28°	–	–	to 27°	–	to 81°
Schönite .	–	–	–	–	to 26°	to 26°	to 26°	–	–	to 26°
Loewite .	above 43°	above 60°	–	–	47°-62°	above 57°	–	–	above 48°	43°-60°
Ashrakanite .	38°-47°	46°-60°	28°-36°	–	to 57°	to 60°	–	–	32°-49°	
Kieserite .	above 37°	–	to 36°	+	32°-38°	–	above 72°	to 33°		
Kainite .	37°-38°	–	to 32°	to 72°	to 55°	–	to 33°			
KCl .	above 55°	–	–	+	to 61°	+				
Glaserite .	above 61°	above 46°	–	–	26°-62°					
Leonite .	37°-62°	–	27°-32°	–						

* The minus sign indicates that paragenesis is excluded between 25° C. and 33° C.

† The plus sign indicates that paragenesis is possible throughout the whole interval of temperature.

Digitized by Google

Data such as these, however, only allow us to judge roughly the temperature which must have existed when a certain bed was laid down. A much more accurate method of determining this temperature is to be found in the state of paragenesis which is observed in the stratum in question. The matter cannot be dealt with in detail in this book; but an examination of the annexed table and of Figs. 20 and 21 will show the applicability of the method.

For example, from the two figures representing the state of affairs at 47° C. and 46° C. respectively, it is clear that if crystallisation takes place at 47° C. langbeinite and astrakanite cannot occur together in the stratum; while, if the temperature sinks lower to 46° C., they may appear as a mixture. Again, at 31·5° C. kieserite and leonite cannot crystallise from the solution simultaneously; if they occur together in a stratum, the deposition must have taken place at 32° C. or above it.

The objection may be made that the effect of pressure might vitiate these conclusions, but van't Hoff investigated this point and showed that even the highest possible pressures would be practically without influence.

It is unnecessary to describe the details of van't Hoff's further researches upon the calcium salts and the borates; the experimental methods employed were similar to those which have already been dealt with. It will be clear that these investigations of van't Hoff and his collaborators have yielded what may be called a "geological thermometer," by the aid of which it is possible to determine the temperature that prevailed in the solution from which certain strata were deposited: and in certain cases this thermometer is so finely adjusted as to enable this temperature to be determined even to within half a degree.

Digitized by Google

CHAPTER V.

COMPLEX SALTS AND COMPLEX IONS.

1. *Introductory.*

It was pointed out in Chapter III. that in some cases the solution of two simple salts containing a common ion may, on crystallisation, give rise to a material the properties of which differ entirely from those of either of the simple salts from which it was formed. This new substance is termed a *complex salt.*

To make the matter clear, an example from analytical methods may be chosen. When potassium chloride is added to an acidulated solution of platinum chloride, a yellow crystalline precipitate is formed which has the composition corresponding to $PtCl_4 . 2KCl$. Since there are six chlorine atoms in this substance it might be expected, by analogy with the behaviour of simple salts, that six molecules of silver nitrate would react with the compound and yield six molecules of silver chloride. In actual practice, however, no silver chloride is formed at all; for the reaction-product is found to have the composition Ag_2PtCl_6. Thus the interaction of the chlorides of platinum and potassium has given rise to a body which no longer possesses the properties of its components but which, instead, has acquired new characteristics. Only the two potassium atoms are replaceable by silver, whilst the platinum appears to be rigidly attached to the remaining chlorine atoms. In order to express this behaviour, the formula of the compound may be written in the form: $K_2(PtCl_6)$; and the deduction may reasonably be drawn that in its dissociation it no longer decomposes into ions of potassium, platinum and chlorine, but ionises into two potassium ions and a third ion having the composition $PtCl_6''$.

This example serves to bring out another point of interest.

Digitized by Google

Not only is there a possibility of complex salt formation, but in addition *complex ions* may exist in a solution. This may appear a matter of little importance at first sight, since the production of ions from salts is a commonplace in chemistry; but the occurrence of complex ions is of more than usual note on account of the fact that the existence of a complex ion does not necessarily imply the existence of the corresponding complex salt in the solid condition. Some complex ions are known to exist in solution though no stable salt can be produced from them. Thus the field of the complex ions is a much wider one than that of the complex salts.

2. *Proofs of the Existence of Complex Ions in Solution.*

There are various methods by means of which the presence of complex ions may be established; and in the present section only a few examples can be given. For fuller accounts the reader is referred to other works.[1] The tests for complex ions may conveniently be grouped under the following heads: (1) Chemical methods; (2) Physical methods; and (3) Electrochemical methods.

1. *Chemical Methods.*—As has already been made clear, the chemical methods depend upon the fact that the formation of a complex ion produces a change in the ionic character of the solution in which the material is dissolved. If dilute solutions of silver nitrate and potassium sulphate be mixed, the resulting liquid will respond to tests for the four ions: silver, potassium, nitrate and sulphate; for the mere mingling of the solutions has not interfered with the ionic properties. On the other hand, when potassium cyanide is substituted for potassium sulphate, a totally different series of phenomena are observed. The addition of potassium cyanide to a solution of silver nitrate leads, in the first place, to the precipitation of a substance which analysis shows to have the composition AgCN; but after this precipitation has been completed, the further addition of potassium cyanide causes the precipitate to dissolve and the solution finally becomes clear again. Evaporation of this solution yields crystals of a compound having the composition AgCN . KCN.

[1] See Jaques, *Complex Ions in Aqueous Solutions*, 1914.

Digitized by Google

A solution of this new compound evidently contains some silver; yet it fails to give many of the ordinary silver reactions. Clearly, the interaction of potassium cyanide and silver cyanide has interfered with the ionic character of the initial salts and has given rise to a new set of ions different from the original three. The potassium ions are still recognisable by the ordinary tests; and, since in any ionic solution the positive and negative charges must balance one another, it is clear that the silver ion and the two cyanide ions must have united to form a complex which carries a negative charge; for no other solution of the problem presents itself. It is therefore reasonable to assume that the ions in the final solution may be represented by $K^{\cdot}$ and $Ag(CN)'_2$, the latter being a complex ion which fails to exhibit the normal reactions of its constituent parts.

Another chemical method of attacking the complex ion problem is suggested by the phenomena of catalysis.[1] A concrete example will serve to make clear the processes employed. The decomposition of hydrogen peroxide proceeds rapidly in presence of iodides; and it has been shown that the catalytic effect is proportional to the concentration of the iodine ion in solution. On comparing the catalytic power of a solution of mercuric iodide with that of a solution of the same concentration of mercuric iodide to which iodine had been added, it was found that there was a marked difference between the two. As the addition of iodine diminished the catalytic powers of the mercuric iodide, the conclusion must be drawn that the halogen in some way reduces the number of iodine ions in the solution; and this is best explained on the assumption that the iodine ions unite with free iodine to form complex ions which have not the catalytic properties possessed by simple iodine ions.

2. *Physical Methods.*—Reference to the influence upon solubility which is exerted by complex ion formation has already been made in a previous section; and it may be well to consider at this point the general aspect of the question. If excess of a salt AB be brought into contact with water, the following dual equilibrium will eventually be established:—

$$\underset{\text{(Solid.)}}{AB} \rightleftharpoons \underset{\text{(Dissolved.)}}{AB} \rightleftharpoons \underset{\text{(Ions.)}}{A' + B^{\cdot}}$$

[1] Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 401; Sherill, *ibid.*, 1908, **43**, 705; Knox, *Trans. Farad. Soc.*, 1908, **4**.

Digitized by Google

This system can be disturbed by the addition to it of more A′ ions or by the removal of some of those already present. The addition of A′ ions to the system will lead to an increase in the rate of combination between A′ and B′ ions, thereby producing more undissociated AB in solution and hence, since the solution is fully saturated with AB already, some AB will be precipitated in the solid form. On the other hand, the removal of some A′ ions will produce a dissociation of some of the dissolved molecules AB, thus disturbing the equilibrium between the solid salt and the dissolved material, and the net result of the process will be the solution of some of the solid salt AB.

The application of these principles to the case of complex ion formation is very simple. Assume that to the system in equilibrium a certain quantity of a salt AC is added, which has the ion A′ in common with the salt AB. AC will be dissociated and thus an extra quantity of A′ ions will find their way into the solution. If no complex ions are formed, the effect of this surplus of A′ ions will be the precipitation of some AB in the solid form; or, in other words, the solubility of AB in the solution will be diminished. On the contrary, if the A′ ions already present in the system are able to form complex ions with the incoming molecules of AC, then the number of A′ ions in the liquid will fall below that which is required for equilibrium; and some of the solid salt must pass into solution in order to make up the deficiency.

Thus in the case of two salts having a common ion, addition of one salt to the saturated solution of the other will decrease the solubility of the first salt and cause its precipitation if no complex ions be formed; but if complex ion formation occurs, the first salt will be more soluble in a solution of the second than it would be in pure water.

The following figures[1] illustrate the point. They represent the solubility in grammes per litre of mercuric cyanide in pure water and in solutions of potassium cyanide of various concentrations:—

Conc. of KCN.	Solubility of $Hg(CN)_2$.	Increase in Solubility.
0·0000	0·44	—
0·0493	0·4855	0·0455
0·0985	0·5350	0·095
0·1970	0·627	0·187

[1] Sherill, *Zeitsch. physikal. Chem.*, 1903, **43**, 705.

Digitized by Google

Examination of the figures will show that the increase in solubility of the mercuric salt goes almost exactly hand in hand with the increase in the concentration of the potassium cyanide, so that the addition of a fixed quantity of potassium cyanide involves the removal from solution of an equivalent amount of mercuric cyanide. This at once suggests that during the process the complex ion $Hg(CN)'_2$ is being formed.

The mode of applying cryoscopic measurements to the complex ion problem is almost self-evident. In dilute solutions each ion acts as an independent particle and exerts on the freezing-point of the solution the same influence as if the ion were a molecule. Thus a dilute solution containing the two salts AB and AC will show a freezing-point depression proportional to the concentrations of the four ions: A′, A′, B· and C·. If, however, complex formation occurs, there will then be only two independent ions in the solution: B· and the complex ion CA'_2; so that in this case the freezing-point depression will only be half the previous value. If the reaction of complex ion formation were an incomplete one, the observed depressions in the freezing-point would lie intermediate between the two extreme values.

The case of hydrochloric acid and mercuric chloride[1] serves to show the type of results which can be obtained by this method. When various amounts of mercuric chloride were dissolved in normal hydrochloric acid, the freezing-points of the solutions were found to be as follows:—

Conc. of $HgCl_2$ in mols. per litre.	Freezing-point °C.	Difference.
0·000	−3·965	—
0·125	−3·785	0·180
0·250	−3·560	0·225
0·375	−3·435	0·125
0·500	−3·350	0·085

From these values several deductions can be drawn. In the first place, complex ions must have been present in the solutions; for otherwise the addition of fresh solute would have depressed the freezing-point regularly, whereas in actual practice each addition of mercuric chloride raises the freezing-point slightly. Second, had each molecule of the mercuric chloride combined directly with one molecule of hydrochloric

[1] Le Blanc and Noyes, *Zeitsch. physikal. Chem.*, 1890, **6**, 401.

Digitized by Google

acid to form a complex ion, then the freezing-point would have remained constant instead of rising. In order to account for the results, it is necessary to assume that at least two hydrochloric acid molecules unite with one molecule of mercuric chloride; so that the complex ion must be either $HgCl'_2$ or must contain an even larger proportion of chlorine.

The distribution of a solute between two immiscible solvents has been utilised in some cases to prove the formation of complex ions; but the method is not capable of extension to every field of the subject, owing to the difficulty of discovering suitable solvents. The best-known instances of its employment are the cases of complex ions formed by the halogens, in which case the rationale of the method is as follows: A solution of bromine in carbon disulphide is shaken with water until equilibrium is established; and the quantity of bromine per litre in the aqueous solution is determined by titration. The same process is then repeated, but in this case a solution of potassium bromide is substituted for the water. The difference between the amounts of bromine abstracted from the carbon disulphide in the two cases must be due to the formation of a complex ion by the bromine and potassium bromide.

In actual practice[1] the method is more complicated owing to the necessity of avoiding the determination of the concentration of the bromine in the carbon disulphide. The carbon disulphide solution was shaken up with pure water both at the beginning and at the end of the series of extractions with potassium bromide solution; and the quantity of bromine theoretically removable by the water under the same conditions as the actual experiments with potassium bromide solution were calculated by extrapolation.

The application of the quartz spectrograph to the study of complex formation[2] led to a new method of detecting the presence of complex ions. It was found that a 25 mm. layer of a N/1000 solution of iodine allowed the ultra-violet spectrum to pass through it with no appreciable loss of intensity. As soon, however, as any potassium iodide was added to the solution, marked absorption was observed,

[1] Roloff, *Zeitsch. physikal. Chem.*, 1894, **13**, 341.
[2] Tinkler, *Trans.*, 1907, **91**, 996; 1908, **93**, 1611.

Digitized by Google

showing that some interaction had taken place between the iodine and the iodide. By this method, not only was it possible to determine the presence of complexes but even to estimate the quantities in which they were present in a given solution.

3. *Electrical Methods.*—There are three electrical methods by means of which the presence of complex ions in a solution may be established; these methods depend respectively upon the results of electrolysis, measurements of ionic migration and determinations of electromotive force. They will now be dealt with in turn.

When a solution of potassium chloride is electrolysed, the metallic ions tend to accumulate at the cathode; while in the case of mercuric chloride the same result is observed. When a solution containing both chlorides is subjected to electrolysis, however, potassium ions collect around the cathode as before, but the solution in the neighbourhood of the anode is found to grow richer in ions containing mercury. Thus the results of electrolysis show that the mercury atoms have become parts of negative ions instead of yielding positive ions as they normally do. The only explanation of this which can be put forward is that a complex ion has been formed.

The transport numbers of ions also serve to throw light upon the formation of complexes, since in such cases the results obtained may appear abnormal at first sight. For example, on examining a solution of cadmium iodide of medium concentration, Hittorf [1] found that the transport number for cadmium was negative, whilst that of iodine was greater than unity. In other words, the current carried by the anion was apparently greater than the total current passing through the solution—which is impossible. When dilute solutions were employed, the values for both cadmium and iodine were found to be positive and less than unity.

To explain these anomalous results, it is necessary to assume that in the cadmium iodide solution a complex has been formed which dissociates into the cation $Cd^{\cdot\cdot}$ and the anion CdI_4''. (Or we may assume the formation of the complex anion without postulating the preliminary production of the complex salt.) In the course of electrolysis an atom of

[1] Hittorf, *Ann. Physik.*, 1859, **106**, 513.

Digitized by Google

cadmium will make its appearance at the cathode, but at the same time another cadmium atom, forming part of the complex anion, approaches the anode. There will therefore be little, if any, change of concentration at the electrodes, as far as cadmium is concerned. As regards iodine, however, the matter is quite different, for every complex anion carries away within it no less than four iodine atoms. Consequently there will be an abnormally large fall of iodide concentration around the cathode. The reversion to more normal results in the case of dilute solutions of cadmium iodide is accounted for by assuming that at high dilutions the complex ions are broken up; so that the case becomes one of the electrolysis of an ordinary ternary electrolyte.

Turning now to the application of electromotive force measurements as a gauge of the presence of complex ions, lack of space forbids a full account of the methods employed, for the experimental difficulties complicate the problem considerably. It will be sufficient in this place to indicate the theoretical basis of the method.

When a silver electrode is placed in a solution of a silver salt the solution pressure of the metal tends to drive silver ions into solution; and consequently a charge accumulates upon the metal owing to the fact that each silver atom in becoming an ion leaves an electron behind upon the electrode. Simultaneously, however, the osmotic pressure of the silver ions in the solution is tending to force them to deposit themselves upon the electrode, where they take up electrons in order to transform themselves into atoms. In due course, equilibrium is established; the solution pressure balances the osmotic pressure; and the electrode has then a definite positive or negative charge which is found to be constant for a given concentration of the solution.

Now it is clear that if this system be disturbed by the removal of silver ions from the solution, an attempt will be made to establish a fresh equilibrium; and under the new circumstances the electrode will acquire a potential different from that which it originally had in the previous equilibrium. Such a removal of silver ions from the solution can be brought about by adding to the liquid some substance which unites with the silver ions to form complexes. Thus when potassium

Digitized by Google

cyanide is added to the silver solution, some of the silver ions are combined with the cyanide to form complex ions; with the result that the silver ion concentration in the solution is altered and a change of potential results at the electrode.

The influence of such operations is much greater than is generally realised. For example, if sufficient potassium cyanide be added to the solution in the copper compartment of a Daniell cell, all the copper ions are removed to form complex ions, with the result that copper begins to dissolve from the electrode and the zinc sulphate in the other compartment is decomposed with the deposition of metallic zinc on the electrode. Thus the formation of the complex ion is signalised by the change in sign of the combination's E.M.F.

3. *The Cobaltammines.*

Among the elements which yield complex salts, the metals of Group VIII. in the Periodic System appear to be the most fruitful; for they give rise to so large a number of complexes containing ammonia that the study of the metalammines has grown into a subject by itself. The cause of this fertility in compound formation has not yet been determined; but one or two suggestive facts may be mentioned in this connection. In the first place, Group VIII. represents one of the "transition groups" of the Periodic System, the others being Group IV. and the Zero Group. Just as carbon in Group IV. yields an abnormal number of valency compounds, so in Group VIII. the elements give rise to an extraordinary series of complex salts. Thus in the two groups the same kind of fertility is displayed, though in the one case ordinary valency conceptions suffice to describe the phenomena whereas among the complex salts of Group VIII. the normal views appear to be insufficient. Secondly, both carbon and the elements of Group VIII. are distinguished by their comparatively small atomic volumes, which may be a factor in the problem. And, finally, while carbon is a truly "amphoteric" element which combines with hydrogen or chlorine to form equally stable compounds, the Group VIII. elements show a capacity for acting either in the form of positive ions or, when merged in a complex, of negative ions. It seems possible that further consideration of these points may

Digitized by Google

suggest some common ground between the chemistry of carbon and that of the elements of the Eighth Group.

The chemistry of the metalammines is so extensive that in the present section only a few of the salient points can be dealt with; and it will be best to confine attention to the case of the complex salts of cobalt.

In its halogen compounds, cobalt behaves almost entirely as a divalent element, though the possibility of trivalency is shown by the existence of cobaltic fluoride, CoF_3. With ammonia, however, the cobalt salts unite to form a series of complex compounds which contain not only three halogen atoms but also a number of ammonia molecules. Representing halogen atoms by X, the following formulæ express the compositions of some of the complex cobalt derivatives:—

$CoX_3 + 3NH_3$; $CoX_3 + 4NH_3$; $CoX_3 + 5NH_3$; $CoX_3 + 6NH_3$.

When the reactions of these complex compounds are examined, it is found that the first compound gives rise to no ions in solution; the second gives two ions, one of which is the ion X; the third produces three ions, of which two are X's; whilst the fourth dissociates into four ions, three of which are X ions. This behaviour can be expressed in the following formulæ, wherein the atoms within the bracket are regarded as forming part of a single large complex ion:—

$$\left[Co^{X_3}_{(NH_3)_3}\right] \quad \left[Co^{X_2}_{(NH_3)_4}\right]X \quad \left[Co^{X}_{(NH_3)_5}\right]X_2 \quad \left[Co_{(NH_3)_6}\right]X_3$$

These formulæ are pure "reaction formulæ," expressing only the differences in behaviour between certain of the atoms in the molecule, and they are independent of any hypotheses with regard to the forces at work upon the atoms. An examination of the formulæ will show that as we pass from left to right there is a steady increase in the number of ammonia molecules within the bracket; and, further, that the entrance of an ammonia molecule results in the extrusion of one X, which takes its place outside the bracket and becomes capable of ionisation.

Turning now to pure hypothesis, it may be assumed that in the case of the compound $(Co(NH_3)_6)X_3$ the six ammonia molecules are placed symmetrically around the cobalt atom in space so as to form an arrangement such as is shown in Fig. 22.

Digitized by Google

This assumption involves no postulates with regard to the forces which retain the atoms in their relative positions, as these are left out of consideration for the present.

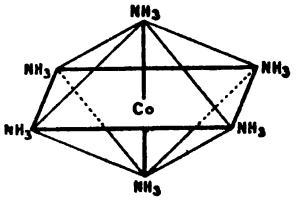


FIG. 22.

Now, let it be assumed that when two of the ammonia groups are replaced within the bracket by two X atoms, the X atoms take up the places previously occupied by the ammonia molecules. In this case there are two possible arrangements in space which are shown in Fig. 23.

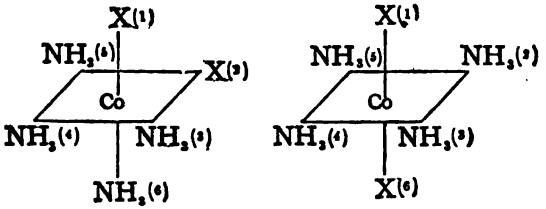


FIG. 23.

In the one case it will be seen that the two X atoms lie at opposite corners of the octahedral grouping, whilst in the other arrangement they lie at two adjacent corners. Thus these spatial arrangements are different from one another, and it might be expected that certain differences would arise between the properties of the two. In actual practice, it is found that cobaltammines of the type

$$\left[Co^{X_2}_{(NH_3)_4}\right]X$$

exist in isomeric forms. Differences in solubility, colour, crystalline form and even chemical properties have been observed.[1] On the other hand, compounds of the types

$$\left[Co^{X}_{(NH_3)_5}\right]X_2 \qquad \left[Co_{(NH_3)_6}\right]X_3$$

display no such isomerism. It seems, therefore, that the assumption of the octahedral grouping of the groups within the complex ion is justified by the results of experiment.

[1] Full references are given in a paper by Werner (*Ber.*, 1907, 40, 15), and later papers by the same author are to be found in the *Berichte*.

Digitized by Google

An even more striking proof of the correctness of this assumption is to be found when the case of the ethylene diamine derivatives of cobalt is considered. Ethylene diamine has the structure: $NH_2 . CH_2 . CH_2 . NH_2$; and since it contains two amino-groups it is evident that one molecule of ethylene diamine might replace two ammonia molecules in the cobaltammine complex ion, giving rise to compounds of the following types in which "en" represents one molecule of ethylene diamine:—

$$\left[\begin{matrix}X\\Y\end{matrix}\!\!>\!Co\ en_2\right]X \qquad \left[\begin{matrix}X\\X\end{matrix}\!\!>\!Co\ en_2\right]X$$

Here X and Y are acidic groups which may be either identical or different in nature.

Applying his octahedral hypothesis to this case, Werner[1] pointed out that molecular configurations would be obtainable from such compounds which would give rise to non-superposable mirror-images and therefore to optical activity. In the figures below, the ethylene diamine chain is represented by the line with the lettering "en" attached to it (Fig. 24).

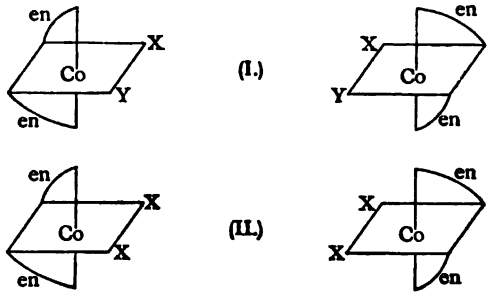


FIG. 24.

Optically active derivatives of compounds of this type have actually been isolated; and this confirmation of hypothesis by experiment marks a very considerable advance in our knowledge of the complex salts of this class. It must again be emphasised that up to this point no assumptions have been made as to the nature of the forces which retain the various atoms within the complex ion. All that has been done is to consider the geometrical relationships of the several groups around the cobalt atom and, basing our theory upon the assumption that the arrangement is octahedral, follow out the train of reasoning and

[1] Werner, *Ber.*, 1911, **44**, 1887, 2445, 3132, 3279; 1912, **45**, 433, 1228.

Digitized by Google

then see if it is confirmed by experiment. The results seem sufficient to support the theory of the octahedral grouping.

There is still one objection which has not been met. These compounds which have been considered all contain nitrogen atoms; and it is well known that nitrogen atoms, when attached to five different groups, are capable of exhibiting the phenomena of optical activity. Though such an arrangement seems unlikely in the cobaltammines, it is well to bring further evidence to show that the optical activity of the complex salts cannot be due to this factor.

Like cobalt, rhodium forms a series of complex salts; and in particular it gives rise to a compound which can be expressed by the formula, $(Rh(C_2O_4)_3)M_3$, in which M represents a metallic atom and C_2O_4 is the chain of oxalic acid:—

—O—CO—CO—O—.

In this case, all the six corners of the octahedron are occupied by the ends of the three oxalic acid chains; no nitrogen atom is present, nor is there an asymmetric carbon atom within the structure. None the less, the compound is optically active. Its spatial configuration is the same as those shown in Fig. 24, with the exception that the oxalic acid chains replace those of ethylene diamine and in addition a third chain unites the points X and Y; and examination will show that such a spatial arrangement is not superposable upon its mirror-image—which is the simplest test for the possibility of the occurrence of optical activity in a compound.*

* The reader can easily test this for himself by cutting out a small square of paper, thrusting a darning-needle through the centre and joining the proper points together with thread or wool to form an arrangement like one of those in Fig. 24, an extra piece of thread being used to connect X and Y. On reflecting this in a mirror and building up a second octahedron identical with the mirror-image, it will be found that the two octahedral arrangements are not superposable on each other.

Digitized by Google

CHAPTER VI.

THE PSEUDO-ACIDS.

1. *Introductory.*

In a rough classification of electrolytes, the first three categories which suggest themselves are—

1. Acids, which give rise to hydrogen ions.
2. Bases, which yield hydroxyl ions.
3. Salts, which dissociate into acidic and basic ions.

To these three classes a fourth must be added: amphoteric electrolytes, which are capable of producing either hydrogen or hydroxyl ions according to the experimental conditions. Amphoteric electrolytes might be sub-divided into two sections: for in one set of these bodies it is found that the same group of atoms gives rise to both hydrogen and hydroxyl ions owing to ionisation taking place in two different ways; while in the second set the hydrogen ions are liberated from one part of the molecule, and the hydroxyl ions from another. Examples of the first class are found among the hydroxides of metals such as lead, aluminium, chromium, beryllium, and tin, which are soluble in both acids and alkalis; while the second class is represented by bodies like amino-acetic acid—

$$NH_2 . CH_2 . COOH$$

the carboxyl group of which furnishes hydrogen ions, while the basic radicle $—NH_2$ forms the origin of the hydroxyl ions.

An additional class of electrolytes was discovered later, the pseudo-acids and pseudo-bases; and the present chapter will be devoted to a description of these acids and their properties. Before entering into details, however, some account must be given of the history of the subject.

When an alkyl iodide is treated with silver nitrite it usually gives rise to two isomeric substances: a nitro-paraffin and an

Digitized by Google

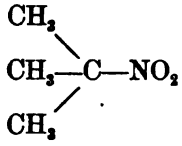
alkyl nitrite. For example, from ethyl iodide, nitro-ethane and ethyl nitrite are obtained :—

$C_2H_5 . NO_2$ — Nitro-ethane.

$C_2H_5 . O . N : O$ — Ethyl nitrite.

With the latter substance we are not concerned here.

The nitro-paraffins were discovered in 1872 by Victor Meyer,[1] and in the course of his investigations he observed that they dissolved readily in alkaline solutions. This pointed to the possibility of their containing a hydrogen atom which was capable of being replaced by a sodium atom; and in accordance with the views current at that time, Victor Meyer inclined to the explanation that the "negative" nitro-group influenced the neighbouring hydrogen atoms so strongly as to make them acidic to some extent. This idea was tested by preparing a tertiary nitro-paraffin, and that substance was found to yield no sodium salt—



Tertiary.

$CH_3—CH_2—CH_2—CH_2—NO_2$

Normal.

An examination of the two formulæ above will show that in the normal substance the carbon atom next the nitro-group has two hydrogen atoms attached to it, whereas in the tertiary body the nearest hydrogen atom is separated from the nitro-group by two carbon atoms. It was therefore assumed that the nitro-group only influenced a hydrogen atom in its immediate vicinity.

In those days, it was taken for granted that the structures of an acid and its salt were analogous, and thus the first formulæ for the alkali derivatives of the nitro-paraffins were written simply by substituting the symbol for the alkali atom in place of one hydrogen—

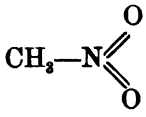
Nitro-ethane.

Sodium derivative.

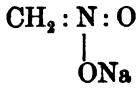
[1] V. Meyer, *Annalen*, 1874, **171**, 1.

Digitized by Google

This view held the field for a considerable period, but in 1888, Michael,[1] in the course of his work on the constitution of acetoacetic ester, was led to challenge the validity of this assumption. According to him, when a metallic atom replaces a hydrogen atom in an organic compound, it will attach itself to an oxygen atom in preference to a carbon atom, owing the greater "negativity" of the former. We cannot enter here into his arguments; a full account of the controversy will be found in Lachman's *Spirit of Organic Chemistry*. Applying Michael's ideas to the case of nitro-methane, we should obtain the following formulæ for the parent substance and the sodium derivative:—



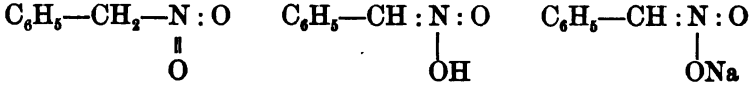
Nitro-methane.



Sodium derivative.

On this assumption, the constitution of the acid cannot be deduced from that of the salt merely by replacing the sodium symbol by the hydrogen symbol; but we must assume that the two bodies differ very considerably in constitution.

In 1895 the problem became still more complicated from the experimental standpoint, for in that year Holleman,[2] Hantzsch and Schultze,[3] and Konowalow[4] independently discovered that nitro-paraffins could be obtained in two isomeric forms, the normal form and the *aci*-form, the latter of which had the same structure as the sodium salts. Thus in the case of phenyl-nitro-methane, the following substances were discovered:—



Normal nitro-paraffin. *Aci*-form. Salt.

This discovery vindicated Michael's views, and the further investigations of Hantzsch carried the subject into a new field.

The substance which Hantzsch and Schultze first examined

[1] Michael, *J. pr. Chem.*, 1888, [2], **37**, 507.
[2] Holleman, *Rec. trav. chim.*, 1895, **14**, 129.
[3] Hantzsch and Schultze, *Ber.*, 1896, **29**, 2193.
[4] Konowalow, *ibid.*, 699.

Digitized by Google

was the phenyl derivative of nitro-methane, which has the structure shown below—

$$C_6H_5—CH_2—NO_2$$

This body is formed by the action of silver nitrite upon benzyl iodide; and in its purification the sodium salt is prepared, and then decomposed by dilute acetic acid or carbonic acid. The substance obtained by this method is a liquid boiling at 225°-227° C.

If, instead of weak acids, fairly strong mineral acids are used to decompose the sodium salt, and care is taken that the temperature of the solution does not rise during the operation, we obtain, instead of the oil, a crystalline body of m.p. 84° C. This substance is the *aci*-form of phenyl-nitro-methane, and has the structure—

$$C_6H_5—CH:\underset{\displaystyle \mid \atop \displaystyle OH}{N}:O$$

which corresponds to the structure ascribed to the sodium salt.

These two bodies differ not only in physical properties, but in chemical character as well, as the following data will show. The normal form of phenyl-nitro-methane is stable when heated; with ferric chloride it yields no immediate coloration; and it dissolves only slowly in alkalis, forming the sodium salt. The *aci*-form of the substance, on the other hand, is labile, and can be converted directly into the normal compound; with ferric chloride it gives at once a red-brown tint; and it dissolves immediately in alkaline solutions, yielding the same salt as the normal form. Thus, if we start from the normal compound we can convert it into the sodium salt, from which we can obtain (by precipitation with mineral acids) the isomeric *aci*-form, and by heating this for a considerable time we can regain the original normal substance by isomeric change.

Now, Holleman[1] showed that if to a solution of the sodium salt of phenyl-nitro-methane we add an equivalent quantity of hydrochloric acid, and determine the conductivity at intervals, we shall find that it rapidly diminishes, which appears to point

[1] Holleman, *Rec. trav. chim.*, 1895, **14**, 121, 129.

Digitized by Google

to the conversion of the *aci*-form into the indifferent, non-conducting normal form. If no secondary reaction took place, it is clear that in the end the conductivity should reach that of a solution of sodium chloride containing the same amount of sodium as the original sodium salt, since the latter is decomposed by the hydrochloric acid to produce sodium chloride. In practice, however, it is found that the isomeric change of *aci*-form into the normal form is accompanied by a slight decomposition of the nitro-body, which produces traces of benzoic acid and nitrous acid; so that the end-conductivity of the solution is influenced by the presence of these electrolytes in addition to the sodium chloride formed in the main reaction. The following figures[1] will give some idea of the velocity of the reaction.

Equimolecular solutions of hydrochloric acid and the phenyl-nitro-methane sodium salt, each at a dilution $v = 32$, were mixed together, producing a dilution $v = 64$. The temperature of the mixture rose from 0° C. to about 2° C., but in the following figures a correction for this has been made: and μ represents the molecular conductivity of the solution at various times.

After	3	minutes	$\mu = 69{\cdot}6$
,,	5	,,	$\mu = 68{\cdot}1$
,,	20	,,	$\mu = 67{\cdot}0$
,,	60	,,	$\mu = 63{\cdot}7$
,,	95	,,	$\mu = 62{\cdot}7$
,,	145	,,	$\mu = 62{\cdot}1$
,,	180	,,	$\mu = 62{\cdot}0$ (constant)

For NaCl under same conditions $\mu = 60$

An examination of the conductivities of solutions of other nitro-methane derivatives showed that the normal nitro-compound in aqueous solution had practically the same conductivity as pure water, whereas the *aci*-derivatives were acids probably stronger than acetic acid.

Let us now summarise what we have dealt with in the foregoing paragraphs. In the first place, it has been shown that derivatives of nitro-methane exist in two isomeric forms, one of which shows neutral properties, while the other isomer is markedly acidic in character. Secondly, the conversion of the neutral body through the *aci*-form into the salt (which is a

[1] Hantzsch and Davidson, *Ber.*, 1896, **29**, 2259.

Digitized by Google

derivative of the acidic form) requires a certain time; this is shown by the different rates at which the two substances dissolve in alkalis: the converse change of the salt into the neutral form of the nitro-compound is also a comparatively slow reaction; this is proved by the conductivity measurements which were given above. Thus in the nitro-paraffin series we have an example of substances which can, by intramolecular rearrangement, become acidic. Such substances Hantzsch defines as *pseudo-acids*. There is another class of compounds which can, by intramolecular change, give rise to basic substances. These Hantzsch terms *pseudo-bases*. It should be noted that Hantzsch lays especial stress upon the point of intramolecular change and not upon the neutral character of one of the isomers. For example, he would include quinone monoxime in the class of pseudo-acids on the ground that intramolecular change takes place in the course of salt formation, the form (I.) being converted into the salt (II.) instead of the salt (III.) being formed as one might expect from the acidic character of the —N . OH group.

$O : C_6H_4 : N.OH$	$NaO . C_6H_4 . N:O$	$O : C_6H_4 : N.ONa$
(I.)	(II.)	(III.)

When a solution of an ordinary acid is mixed with that of a base, the velocity of neutralisation is immeasurably rapid; but in the case of a pseudo-acid, since intramolecular change must occur and convert the pseudo-acid into the *aci*-form before neutralisation can begin, it is evident that the neutralisation will not be an "instantaneous" reaction, but will be governed by the velocity of the intramolecular change. This Hantzsch defines as *slow neutralisation*.

2. *Hantzsch's Criteria.*

In one of his earlier papers on the subject of pseudo-acids, Hantzsch[1] put forward a series of criteria by means of which he suggested that it was possible to establish whether or not a substance was a pseudo-acid. Some of these criteria have since been abandoned as inapplicable; but we may give the original list here, reserving a discussion of each for the later sections of this chapter.

[1] Hantzsch, *Ber.*, 1899, **32**, 575; 1906, **39**, 2109.

Digitized by Google

I. When a hydrogen compound shows slow neutralisation phenomena it is a pseudo-acid.

*II. When a hydrogen compound which itself shows little or no conductivity, produces a neutral alkali salt which is either not hydrolysed or only exhibits slight hydrolysis, then this salt has a constitution different from that of the original hydrogen compound—*i.e.*, the latter is a pseudo-acid.

III. When a colourless hydrogen compound (which when dissolved in water gives a colourless solution) yields coloured ions and alkali salts which retain their colour in the solid form, it is a pseudo-acid.

†IV. If in conductivity measurements of a tautomeric substance it is found that the temperature-coefficient is abnormally large and increases with a rise in temperature; or if the dissociation constant varies to an abnormal extent with change in temperature, it indicates that the substance in question is a pseudo-acid.

V. (*a*) If a substance which in its normal form contains no hydroxyl group can be induced to react with acetyl chloride or phosphorus pentachloride with the liberation of hydrochloric acid, it is a pseudo-acid.

*(*b*) If a hydrogen compound does not form a salt by direct addition of ammonia but only does so indirectly—*i.e.*, in conjunction with water—then the hydrogen compound is a pseudo-acid.

VI. The existence of abnormal hydrates ‡ in the case of tautomeric bodies is a chemical indication that the corresponding water-free substances are pseudo-acids which only produce salts indirectly by the previous formation of an addition-compound of the hydrate type.

*These criteria have since then been proved to be invalid.

†These criteria are of very limited application.

‡Abnormal hydrates are defined by Hantzsch as those which are not formed by direct addition of water to the non-hydrated substance, but are produced only after the original substance has undergone chemical change, *e.g.*, when it is precipitated from salts, etc.

Digitized by Google

* VII. The molecular conductivity of all electrolytes in aqueous-alcoholic solution is reduced if the alcohol content of the solution be increased while the degree of dilution is kept constant; but the diminution of the conductivity of true acids is greater under the same conditions than is the case with pseudo-acids.

It should be expressly stated that Hantzsch admits that no one of these criteria in itself is a conclusive proof of the presence of a pseudo-acid. All that can be said for them is that if a compound agrees with several criteria, then the probability is that it is a pseudo-acid. Further, the various criteria differ in decisiveness. Hantzsch in one of his papers[1] laid especial stress upon the neutralisation phenomena, the ammonia reaction, and the formation of coloured ions by colourless parent substances; while he attached much less importance to the other criteria.

In the succeeding sections the various criteria will be taken up in turn and an account will be given of the criticisms which they have evoked.

3. *The Phenomena of Slow Neutralisation.*

Some description of the slow neutralisation phenomena has already been given in the first section of this chapter. Experimentally, the question may be approached from either of two points. In the first place, we may prepare a solution of the sodium salt of a nitro-paraffin, say nitro-ethane, and add to it the molecular equivalent of hydrochloric acid. If the dilution be considerable and the temperature be kept in the neighbourhood of zero, it is found that at the moment of the addition the conductivity is considerably higher than that of a solution of sodium chloride under the same conditions. This increase in conductivity above that of a common salt solution is to be attributed to the presence of the *aci*-form of nitro-ethane, which results from the double decomposition—

$$CH_3 . CH : NO . ONa + HCl = NaCl + CH_3 . CH : NO . OH$$

The presence of the *aci*-form is also shown by the fact that at the moment of mixing the two solutions, the mixture is acid

[1] Hantzsch, *Ber.*, 1906, **39**, 2109.

* This criterion is of very limited application.

Digitized by Google

and gives a coloration with ferric chloride. After a few hours, however, the conductivity sinks to that of an equivalent solution of pure sodium chloride; while simultaneously the solution loses its acid properties and ceases to give any ferric chloride coloration. This is to be attributed to the conversion of the *aci*-form into the neutral nitro-compound—

$$CH_3 . CH : NO . OH \rightarrow CH_3 . CH_2 . NO_2$$

The second method depends upon the slow formation of the nitro-paraffin salt. Equimolecular aqueous solutions of nitro-ethane and sodium hydrate are mixed together; and it is found that the conductivity does not immediately attain that of the sodium salt of nitro-ethane. Whence it may be deduced that salt formation is not instantaneous, but requires a measurable time to complete.

Now, though the slow neutralisation phenomena give a clue to the presence of a pseudo-acid, it must not be assumed that the converse proposition also is true. Because a body does not show slow neutralisation we are not entitled to take for granted that it is not a pseudo-acid. It is clear that what we actually measure in the case of slow neutralisation is the rate of change of the normal form into the *aci*-form, or *vice versâ*. But if this change took place with very high velocity, it is quite possible that it might be complete before we could measure the conductivity. In this case, we might actually be dealing with a pseudo-acid, but conductivity measurements might lead us to suppose that we had a true acid instead. Thus this criterion of Hantzsch holds good only if we obtain positive results. If the conductivity measurements do not demonstrate the presence of a pseudo-acid we are not entitled to assume that the substance is not pseudo-acidic.

4. *Abnormal Hydrolysis.*

The evidence upon which Hantzsch [1] was induced to put forward this criterion for pseudo-acids may best be given in his own words. "The potassium salt of dinitro-ethane reacts completely neutral and is not more hydrolytically dissociated than, *e.g.*, potassium chloride. Such salts, however, as I will show by numerous examples, are derived from strong or

[1] Hantzsch, *Ber.*, 1899, 32, 579.

Digitized by Google

at least moderately strong acids (of the same strength as the acetic acid group) which have a clearly marked acidity; for very weak acids produce hydrolytically dissociated salts with an alkaline reaction. Now free dinitro-ethane has not a medium, or even a very small, dissociation constant; it has absolutely no measurable dissociation constant at all. Thus it is not merely an acid weaker than very weak acids like hydrocyanic acid or phenol; it is not an acid at all. Now if it, acting as an acid, could produce a salt $CH_2 . CK . (NO_2)_2$, then this salt would be hydrolysed to a greater degree than even potassium cyanide or sodium phenolate. Since, however, the actual so-called salts of dinitro-ethane show absolutely no hydrolysis, they cannot be derived from unaltered dinitro-ethane, but must be produced from an isomeric acid form, iso-dinitro-ethane."

Unfortunately for this reasoning, it was shown by Kauffmann[1] that it is in contradiction with the Law of Mass Action. Assuming this law, it can be proved that in spite of salt formation being accompanied by intramolecular change the hydrolysis of the salt will be normal. Thus this criterion falls to the ground.

5. *Colour-Change in Passing from Pseudo-acid to Salt.*

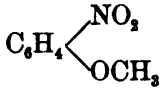
It will be recalled that Hantzsch laid down as one of his criteria, that if a colourless hydrogen compound gives rise to coloured ions and coloured solid alkali salts, then it is a pseudo-acid. At the time this was first put forward, the only evidence in favour of it was physico-chemical, and no purely chemical data were forthcoming for a considerable period. In order to prove chemically that a compound is capable of existing in two isomeric forms it is essential to isolate two isomeric derivatives from the parent substance, and it was not until 1906 that Hantzsch and Gorke[2] were enabled to announce that this criterion had been put upon a purely chemical basis by the isolation of two methyl ethers of *o*-nitro-phenol. These two bodies resembled in character the isomeric ethers of phenyl-

[1] Kauffmann, *Zeitsch. physikal. Chem.*, 1904, 47, 618; *cf.* Euler, *Ber.*, 1906, 39, 1607.

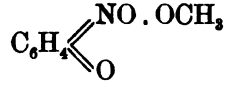
[2] Hantzsch and Gorke, *ibid.*, 1073.

Digitized by Google

nitro-methane, and to them the following formulæ were ascribed:—



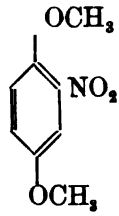
Normal ether.



Ether of *aci*-form.

The first substance is a colourless compound, while the *aci*-ether has an intense red tint. Thus the intramolecular change which produces the *aci*-form from the normal nitrophenol is accompanied by a change in colour.

Some remarks of Hantzsch [1] in reference to the auxochrome view of colour in this connection led to a somewhat prolonged controversy with Kauffmann,[2] into the details of which we need not enter here. Kauffmann adduced the case of the dimethyl ether of nitro-hydroquinone, which, according to him,[3] is capable of giving both coloured and colourless solutions, though, as can be seen from its formula, no isomeric change is probable in the molecule—



Kauffmann stated that in ligroin solution the substance is colourless; but that on allowing it to crystallise, intensely yellow needles are obtained. Other solvents, especially associating solvents, gave pale yellow solutions, while dissociating solvents, such as glacial acetic acid, water or alcohol, gave more deeply coloured solutions. Thus, according to Kauffmann, "in dissociating solvents, the solute shows its natural properties most clearly; in associating solvents, on the contrary, it is in a state of strain". This last phrase will, of course, appear to furnish a complete explanation or to be mere words, according to the reader's prejudices. Hantzsch [4] in his

[1] Hantzsch, *Ber.*, 1906, **39**, 1084.

[2] Kauffmann, *ibid.*, 1959, 4287; 1907, **40**, 481, 4547; see also Hantzsch, *ibid.*, 1906, **39**, 3072; 1907, **40**, 1556, 1572,; 1908, **41**, 1214.

[3] Kauffmann, *ibid.*, 1906, **39**, 4240. [4] Hantzsch, *ibid.*, 1907, **40**, 1556.

Digitized by Google

reply pointed out that Kauffmann's assumption was not in accordance with our experience. In dissociating solvents we do not find a substance showing its "normal" behaviour, for in such solutions we get dissociation or addition-compound formation. Hantzsch then proceeded to examine the molecular weight, colorimetric value and molecular refraction of nitro-hydroquinone dimethyl ether in various solvents, and found that it was probable that the yellow solutions of the body contained molecular complexes. If this be the case, and since the solid substance is also yellow, it seems fair to assume that the yellow colour sometimes shown by the substance is due to the formation of complexes and is not inherent in the molecule; and hence Kauffmann's case falls to the ground.

Further evidence in this direction is furnished by some work of Blaise[1] who showed that when glutaconic ester—

$$COOEt—CH : CH—CH_2—COOEt$$

is treated with sodium ethylate, it gives a yellow colour, whereas if a homologue which contains no free hydrogen atom is treated with sodium ethylate no colour is developed. This points to the wandering of a hydrogen atom during the addition of the ethylate, the addition-compound being supposed to have the following structure:—

$$COOEt—CH : CH—CH : C\begin{matrix}ONa\\OEt\end{matrix}$$

It seems probable, on the evidence before us, that this criterion of a pseudo-acid is valid.

6. *Abnormal Temperature Coefficients.*

In his original paper on the pseudo-acids, Hantzsch[2] expressed this criterion in the following words: "Temperature coefficients of conductivity which are abnormally large and which increase with rise in temperature, as well as degrees of dissociation and dissociation constants which vary to an abnormal extent with temperature change, indicate in the case of tautomeric bodies the presence of ionisation-isomerism".

[1] Blaise, *Bull. soc. chim.*, 1903, **29**, 1028.
[2] Hantzsch, *Ber.*, 1899, **32**, 579.

Digitized by Google

It will be seen that the kernel of the question lies in the word abnormal; and from the polemics of Hantzsch and Euler, it appears that this expression is capable of rather wide interpretations.

Hantzsch[1] based his views upon the assumption that true acids, which do not alter their constitution, show an increase of conductivity with rise in temperature; but that this increase is small and is to be considered as due to an increase in ionic mobility rather than to an increase in the degree of ionisation. Further, according to him, in the case of true acids, the conductivity temperature coefficients diminish with rise in temperature. Finally, the dissociation constants of acids of unchangeable constitution are not dependent to any great extent upon temperature, since in the aromatic acids between 0° C. and 25° C. the variation does not usually exceed about 10 per cent., sometimes positive and sometimes negative. In contrast to this behaviour, Hantzsch placed that of the pseudo-acids which, according to him, between 0° C. and 25° C. show an increase of 100 per cent. or more in the constant.

In his criticism of Hantzsch's views, Euler[2] pointed out that a comparison of the temperature coefficient of a pseudo-acid like phenyl-nitramine with those of true electrolytes such as aniline or phenol shows that the latter bodies have a much higher coefficient.

Hantzsch in his reply[3] objected to the comparison of a weak electrolyte with such a substance as dinitro-methane, which is ten times as strong as acetic acid. He admitted, however, that nitroform, which is undoubtedly a pseudo-acid, has almost the same low coefficient of temperature as hydrochloric acid.

Without going further into the question, it is evident that this criterion cannot stand by itself, but can be used only in support of other evidence. It should be noted, however, that Hantzsch expressly stated this in his earlier papers: none of his criteria in itself is sufficient to *prove* the presence of a pseudo-acid; all that can be done is to show the probability that a substance belongs to this class.

[1] Hantzsch, *Ber.*, 1899, 32, 579.
[2] Euler, *ibid.*, 1906, 39, 1607.
[3] Hantzsch, *ibid.*, 2098.

Digitized by Google

7. *The Ammonia Reaction.*

This criterion depended upon the rate of precipitation of an ammonium salt from a solution in absolute benzene. Solutions of the pseudo-acid and of ammonia in benzene were mixed together under certain conditions and it was found that a slow precipitation of ammonium salt took place, which was in sharp contrast to the immediate precipitation produced when benzoic acid was substituted for the pseudo-acid. Further investigations, however, convinced Hantzsch[1] that the factor of super-saturation entered so powerfully into the question as to make the criterion of little value.

8. *Abnormal Hydrates.*

When a substance forms a hydrate it is usually assumed that direct addition of water to the molecule occurs; but in certain cases it is possible that before water can attach itself to the substance, the latter body must undergo intramolecular change. Such hydrates are defined by Hantzsch[2] as "abnormal," and their presence can be taken as a proof that the compounds which yield them are capable of tautomeric change. Suppose that a substance is capable of tautomeric change and gives rise to a hydrate. By substitution the structure of the molecule can be altered so as to prevent this tautomerism, while the general character of the substance is still retained. If this derivative gives no hydrate, then we should be justified in assuming that the hydrate formation was in some way bound up with the possibility of tautomerism; and we might suppose that tautomeric change must occur before the hydrate could be formed. In this case, of course, the parent substance would be a pseudo-acid. Instead of the addition of water, we might utilise the addition of alcohol as a test; the reasoning in the case of alcoholates is the same as that used for hydrates. It will be seen that the possibility of applying this criterion is very limited.

9. *Conductivity in Aqueous-Alcoholic Solutions.*

Hantzsch and Voegelen[3] observed that if a pseudo-acid and a real acid be dissolved in mixtures of alcohol and water,

[1] Hantzsch, *Ber.*, 1907, **40**, 3084. [2] *Ibid.*, 1899, **32**, 579.
[3] Hantzsch and Voegelen, *ibid.*, 1902, **35**, 1001.

Digitized by Google

the dilution of the solution being kept constant while greater percentages of alcohol are added, then the diminution of the conductivity of the true acid with increase of alcohol is less than the falling off in the dissociation of the pseudo-acid. A concrete example will make the point clear. Suppose the conductivities of violuric acid and lævulinic acid are compared at v_{64}. The two acids are approximately of the same strength, for with violuric acid K = 0·0027, while lævulinic acid has K = 0·0024.

Percentage of alcohol in solution	0%	25%	40%	50%	75%	100%
Violuric acid μ_{64}	14·50	6·53	4·13	2·91	0·90	0·23
Lævulinic acid μ_{64} . . .	13·85	4·65	2·35	1·49	0·32	—

An examination of the figures will show that when the solution contains say 40 per cent. of alcohol, in the case of violuric acid the original figure 14·50 has fallen to 4·13, whereas in the case of lævulinic acid the fall has been greater, from 13·85 to 2·36. Thus by the same change of character of the solutions we have produced a drop of 10·37 units in the case of violuric acid and 11·49 units in the case of lævulinic acid. In other words, the pseudo-acid has shown less decrease in conductivity than the true acid.

This criterion is not applicable in every case, for Euler [1] has shown that phenyl-nitramine and acetic acid give practically the same results, as the following figures for K . 10^6 prove :—

	Water.	40 Per Cent. Alcohol.
Phenyl-nitramine	17·5	1·26
Acetic acid .	17·8	1·86

To this, Hantzsch [2] retorted that the criterion does not necessarily hold in the case of every pseudo-acid; all that we need say is that if a substance agrees with it, then that substance is a pseudo-acid. If the substance does not show the phenomena it may or may not be a pseudo-acid; and further tests must be applied if we are to determine its nature.

10. *The Refractometric Method.*

In the foregoing sections we have dealt with the criteria laid down by Hantzsch in the course of his researches on the

[1] Euler, *Ber.*, 1906, 39, 1607. [2] Hantzsch, *ibid.*, 2098.

Digitized by Google

pseudo-acids. There remains one other method, devised by Muller,[1] which enables us to determine whether a pseudo-acid is present. It is well known that in many cases it is possible to calculate the refractive index of a given substance by simply adding together a series of known factors which correspond to the atoms and linkages of the substance's molecule. This method breaks down when tautomeric change is possible within the molecule, as then we might get an observed value corresponding to either form of the compound's structure or to a mixture of the two forms. In such cases it is often possible to determine the exact constitution of the substance observed, even when it consists of a mixture of two isomerides.

Now suppose that we have an acid RH yielding a sodium salt RNa which is formed without intramolecular transposition, it is clear that if we take the difference between the refractivities of RH and RNa under identical conditions this difference will depend entirely upon the H and Na, that is, the difference will be a constant for all normal acids. This constant difference has been found to be approximately 1·6. Let us now consider the case of a pseudo-acid. Here, not only have we the replacement of hydrogen by sodium, but in addition we have an alteration of the compound's structure due to the change of the pseudo-acid into the *aci*-form previous to salt formation. This change in structure is accompanied by a considerable alteration in refractivity, so that in the case of the pseudo-acid we should expect to find that the difference between the refractivity of the parent substance and that of the salt would diverge considerably from the normal difference of 1·6 units. This has actually been found to be the case by Muller. Taking into account the accuracy with which refractivity measurements can be made, this method of proving the presence of a pseudo-acid appears to possess considerable advantages over most of the others.

11. *Conclusion.*

We have now discussed the various criteria which may be applied to determine whether or not a given substance

[1] Muller, *Compt. rend.*, 1902, **134**, 664; see also his article in *Recents progrès de la chimie* (2nd Series), 1906, p. 40.

Digitized by Google

should be ranked as a pseudo-acid or as a normal acid. Some of Hantzsch's original suggestions have proved of no value, and it is clear that others are either of little use or of very limited application. The most valuable ones seem to be the phenomena of slow neutralisation, the change of colour in passing from a pseudo-acid to its alkali salts, and the refractometric method. Of less importance are the temperature coefficients, the formation of abnormal hydrates, and the conductivity decrease in aqueous-alcoholic solutions. The ammonia reaction and the supposed abnormal hydrolysis of salts of pseudo-acids have been found to be worthless.

In connection with the pseudo-acids, attention may be drawn to the case of tetranitro-methane.[1] Under normal conditions, this substance appears to exist in the pure nitro-form, $(NO_2)_3C.NO_2$; but in presence of amines or alkyl sulphides it seems to be slowly converted into trinitro-nitrito-methane, $(NO_2)_3C.O.N:O$; for it gives exactly the same colour reactions as are observed in the case of alkyl nitrites of the type, $R.CH_2.O.N:O$. This case seems to be a half-way stage towards pseudo-acidity.

[1] Harper and Macbeth, *Trans.*, 1915, **107**, 87; Macbeth, *ibid.*, 1824.

Digitized by Google

CHAPTER VII.

THE THEORY OF INDICATORS.

1. *Ostwald's Ionic Hypothesis.*

THE history of the indicator theory is of interest from more than one standpoint. In the first place, it brings out clearly the fact that, without injury to the science, it is impossible to split up chemistry into the water-tight compartments of the organic, inorganic and physical sections; and it suggests that the training of pure specialists, no matter what their eminence may be, is not an infallible remedy against errors. In the case of the chemistry of indicators, this tendency towards specialisation retarded our knowledge for a considerable number of years. Since among organic chemists the problem of chemical structure is pre-eminent, the investigations of indicators from this side were almost wholly devoted to the elucidation of the chemical constitution of the parent substances; and their behaviour on salt formation was hardly brought under consideration at all. On the other hand, the average physical chemist—and even more so the physical chemist of the Ostwald school—appeared to be indifferent to the problems of pure organic chemistry; and his interest in the indicator question was directed chiefly toward inquiries as to the behaviour of ions.

Secondly, the history of indicators demonstrates clearly that even in present-day science the influence of authority counts for a good deal. Had Ostwald's indicator hypothesis been put forward by an unknown man, it is doubtful if its improbabilities would have passed without examination for a whole decade.

Thirdly, the conservatism of the scientific mind can be traced in the fact that in some compendious works on chemistry the old erroneous hypothesis was still being described as correct, even ten years after its basis had been destroyed by careful investigations.

In order to understand the chemistry of indicators, it is

Digitized by Google

necessary to go back to the researches of Ostwald[1] upon the colour of ions. From an examination of the solutions of a number of coloured salts, he was able to show that the absorption spectra of dilute solutions of salts containing the same coloured ion are identical. For instance, the dilute solutions of the permanganates of lithium, cadmium, aluminium and nickel all contain a common absorption band which is evidently characteristic of the permanganate ion. This establishes the fact that when any salt yielding a given coloured anion is completely dissociated in solution, the tint of the anion is independent of the nature of the cation.

As a sequel to these observations, Ostwald put forward his hypothesis as to the indicator mechanism.[2] His fundamental postulate was that the colour changes observed among indicators were due to the dissociation of the indicator molecule into its ions or the recombination of the ions to form an undissociated molecule. To account for the actions of acid and alkali upon such an indicator as phenolphthalein, he advanced the following suggestion. Phenolphthalein is a very weak acid. Consequently, in presence of stronger acids (or even of water) it is practically undissociated; and since the undissociated molecules are colourless, the solution remains untinged. When a strong base such as sodium hydroxide is added to the aqueous solution, the sodium salt of phenolphthalein is formed; and it becomes strongly dissociated, yielding the coloured anion of phenolphthalein, which thus tints the solution with the same colour, no matter what cation is present. The addition of an acid to this coloured solution causes an increase in the hydrogen ion content of the liquid, with the result that these hydrogen ions combine with the phenolphthalein anions, producing colourless phenolphthalein molecules once more.

When phenolphthalein is added to a concentrated solution of sodium hydroxide, it is found that no colour at all is developed. On the ionisation hypothesis this was accounted for by the assumption that the presence of the large excess of sodium ions in the solution tended to drive back the dissociation of the sodium salt of phenolphthalein, so that only a few of the dissociated, coloured ions of phenolphthalein found their way into solution.

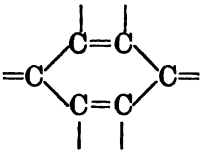
[1] Ostwald, *Zeitsch. physikal. Chem.*, 1892, 9, 579.
[2] *Ibid.*; see also his *Foundations of Analytical Chemistry*, p. 118.

Digitized by Google

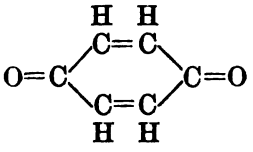
Ostwald's acquaintance with the chemistry of indicators must have been of an extremely sketchy character; for otherwise he would have been aware of the fact that the solid salts of phenolphthalein, for example, are strongly coloured compounds; so that the mere combination of ions to form the undissociated sodium salt would not be sufficient to cause the disappearance of colour. None the less, his authority was apparently sufficient to prevent any further investigation of the indicator problem until the researches of Hantzsch upon the pseudo-acids began to throw light upon the matter from an entirely new angle. As will be seen in the next section, the true explanation of the indicators' behaviour was established mainly by the work of organic chemists.

2. *The Intramolecular Change Theory.*

In order that the indicator problem may be understood, it is necessary to deal very briefly with a relationship which has been established between the presence of a certain chemical grouping—the quinonoid structure—in a molecule and the exhibition by that molecule of colours visible to the eye. This quinonoid structure may be represented thus:—



Quinonoid structure.



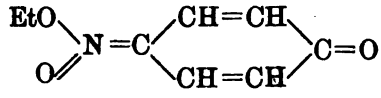
Quinone.

and the name is derived from that of quinone, which contains this molecular arrangement. It is, of course, not essential for the production of colour that a quinonoid grouping should be present in a molecule; for other chromophores are known such as the azo-group, —N : N—, or the diketo-group, —CO . CO—; but the results of a very large number of observations show that if a derivative of the benzene series while containing no other chromophore, displays colour, then its formula can be rearranged into a quinonoid form; and the deduction has been drawn that the molecules actually exhibiting the coloration are quinonoid in structure. Now benzene derivatives having the ordinary benzenoid constitution are not coloured to the eye

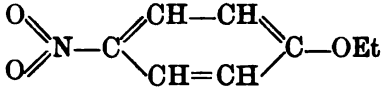
Digitized by Google

unless they contain some chromophoric group; so that if a compound of this type develops visual coloration it is safe to conclude that its structure has undergone rearrangement into the quinonoid form.

An example will make the matter clear. From a nitrophenol, two isomeric ethers may be obtained, one of which is colourless while the other is intensely yellow. The yellow isomer is labile and is readily transformed into the stable variety. Taking the case of para-nitrophenol as an instance, the two isomeric ethers would be represented thus:—



Yellow isomer.



Colourless isomer.

and it will be seen that the transformation of the coloured compound into the colourless isomer is accompanied by a disappearance of the quinonoid structure which forms the main part of the yellow ether's molecule.

From what has been said in the last chapter, it will be evident that this is merely a case of pseudo-acidity; and that the one ether is derived from the *aci*-form whilst the other is produced from the normal form of the nitrophenol.

It is now possible to turn again to the indicator problem. For rather more than ten years Ostwald's ideas held the field, and it was not until 1903 that they were challenged by several investigators[1] who brought forward their objections in that year. For the sake of simplicity, attention may here be confined to the case of phenolphthalein, since this substance played the greatest part in the course of the discussion.

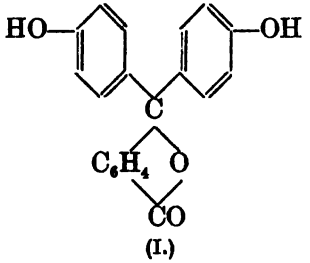
Stieglitz pointed out that in view of the intimate connection between colour and chemical constitution which had been common knowledge for over a quarter of a century, it was most improbable that phenolphthalein, having no chromophoric group in its molecule, should become intensely red merely by

[1] Stieglitz, *Amer. Chem. Soc.*, 1903, **25**, 112; Kremann, *Zeitsch. anorgan. Chem.*, 1903, **33**, 87; Bredig, *ibid.*, **34**, 202.

Digitized by Google

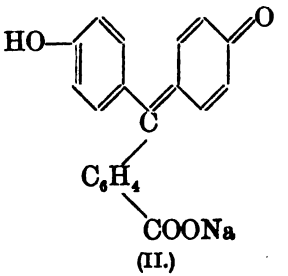
dissociation into ions; and he drew attention to Hantzsch's work on the pseudo-acids as furnishing parallel cases wherein a colourless compound develops colour on being treated with alkali.

This paper brought the subject into a new orientation. Instead of mere ionisation being blindly accepted as the root-cause of indicator colours, it became clear that a much more probable explanation might be furnished by assuming that the origin of the colour-changes was to be sought in intramolecular rearrangements in the structures of the indicators. According to Stieglitz, undissociated phenolphthalein has the constitution (I.), which contains no quinonoid grouping and is visually colourless. The formation of the sodium salt leads, on his hypothesis, to a rearrangement of structure which gives rise to the quinonoid grouping shown in (II.). As Hantzsch pointed out later, the colourless character of phenolphthalein in concentrated alkaline solutions may be accounted for by the presence of a salt having the structure (III.), which, like that of phenolphthalein itself, contains no quinonoid grouping.



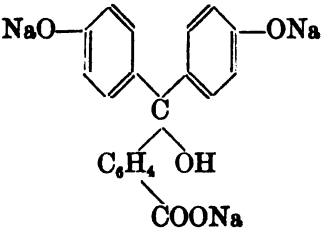
(I.)

Phenolphthalein (colourless).



(II.)

Monosodium salt (coloured).



(III.)

Trisodium salt (colourless).

Digitized by Google

But already evidence had come to light which proved the insufficiency of the ionic hypothesis. The red solution produced by adding a base to phenolphthalein slowly loses its colour on the addition of a large quantity of dilute alkali; and when this alkaline solution is neutralised with acetic acid at low temperatures, no development of colour is observed. On boiling the solution, however, the red colour reappears.[1]

Again, when the methyl ester of phenolphthalein was prepared,[2] it was found to be scarlet in colour, although in the process of esterification the most powerful ionogenic centre in the molecule (the carboxyl radicle) is put out of action. This methyl ester retains its colour for a time in presence of acids; but becomes decolorised in aqueous solution after standing for twelve hours. The decolorisation proceeds much more rapidly in alcoholic solution.

Then, finally, the reactions between bases and compounds of the phenolphthalein series are not instantaneous ones—as they would be were mere ionic processes alone involved—but require instead a measureable time for their completion. When an excess of sodium hydroxide is added to a solution of tetrabromophenolphthalein, the mixture shows a very high electrical conductivity; but this gradually diminishes until, after about forty minutes, it reaches a minimum value at which it remains approximately constant.[3] This behaviour, which is exactly parallel to the behaviour of a pseudo-acid, is quite inexplicable on the purely ionic hypothesis; and the slow decolorisation of the methyl ester of phenolphthalein in aqueous solution shows that in this case also some process is involved which requires time for its accomplishment.

These facts completely destroy the Ostwald hypothesis.* They not only cannot be explained by it; but some of them actually are the very reverse of what could be deduced from its application. For example, if ionisation be the cause of the

[1] Green and Perkin, *Trans.*, 1904, **85**, 398.

[2] Green and King, *Ber.*, 1906, **39**, 2365; Hantzsch and K. Meyer, *ibid.*, 1907, **40**, 3480.

[3] K. Meyer and Hantzsch, *ibid*, 3479.

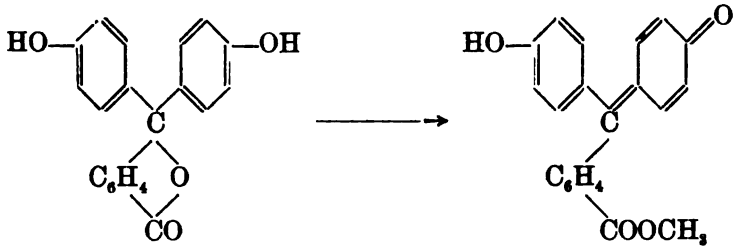
* Ostwald's knowledge of organic chemistry was apparently insufficient to allow him even to appreciate the bearing of these researches upon his ionic hypothesis, for in his *Grundriss der allgemeinen Chemie* (4th edition, 1909), he gives the ionic view as the correct one.

Digitized by Google

colour of red phenolphthalein, how is it possible that the scarlet ester should show a tint in acid solution and yet tend to become colourless in aqueous solution?

When the theory of intramolecular change is applied to these cases, it is found that a satisfactory explanation can be reached. In the case of the first set of experiments, the following process evidently takes place. The preliminary appearance of colour when a base is added to phenolphthalein is due to the change from the benzenoid to the quinonoid structure represented in the formulæ below. Further addition of alkali brings into existence the benzenoid trisodium salt, which is colourless. Neutralisation of the solution containing this salt by means of acid in the cold simply displaces the sodium atoms from the hydroxyl groups without bringing about any change in constitution; so that the colourless benzenoid form of the nucleus remains unchanged. When heat is applied, however, the compound loses a molecule of water and reverts to the usual monosodium salt of phenolphthalein, so that the solution becomes coloured. The formulæ on p. 120 will make the various changes clear.

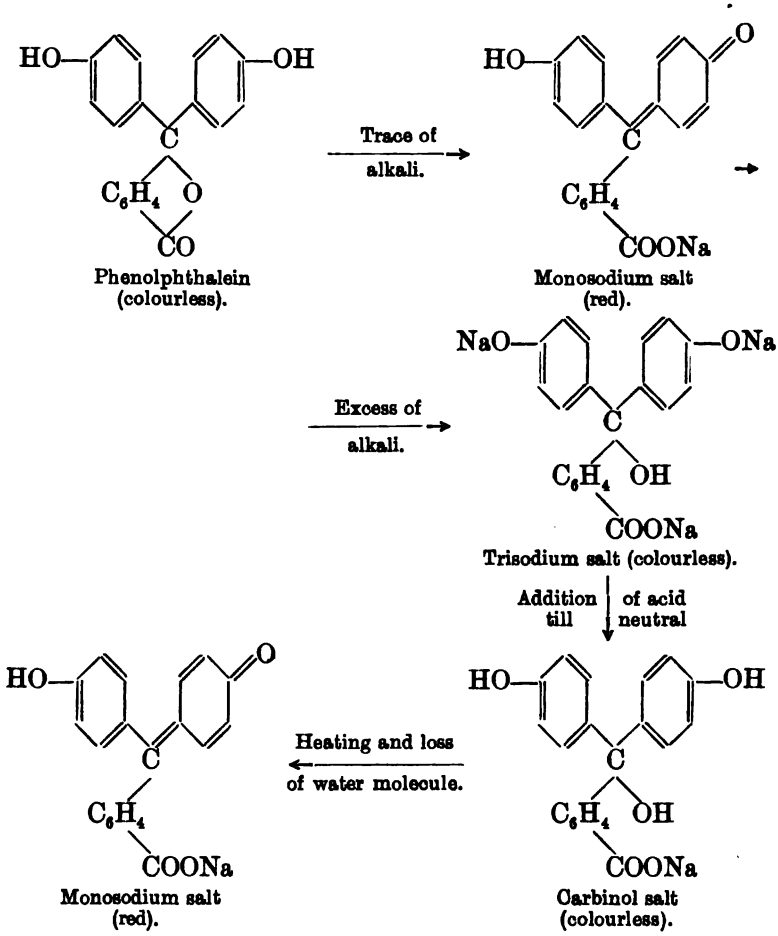
Turning to the case of phenolphthalein ester, the esterification of the carboxyl radicle forces the production of the quinonoid form, since the lactonic ring is opened:—



Phenolphthalein (colourless). Ester (red).

In presence of acid, the ester is not immediately hydrolysed, so the red tint persists for a time. In aqueous solution, hydrolysis takes place on standing, with the result that the compound eventually reverts to the benzenoid lactonic form; but owing to the presence of the water of the solvent, the elimination of a water-molecule to form the lactone is not a

Digitized by Google



swift process. On the other hand, when alcohol is used as a solvent, there is very little back-reaction and consequently the system changes into the benzenoid type with much greater rapidity.

In a later paper Hantzsch,[1] upon whose pseudo-acid researches the modern chemical theory of indicators depends, summarised the objections to the Ostwald hypothesis. In the first place, it is a well-established fact that all salts derived from colourless bases and colourless acids of unalterable structure yield only colourless ions. Secondly, coloured ions are formed only from salts which in the undissociated condition are already

[1] Hantzsch, *Ber.*, 1906, **39**, 1084.

Digitized by Google

coloured.* Thirdly, colourless compounds which give rise to coloured ions have been proved to undergo structural change during the process. From these facts it is evident: (1) that colour production is absolutely independent of ionisation, and (2) that the production of coloured from colourless compounds necessitates a structural change in the molecule. The important point in the indicator question is therefore the possibility of such intramolecular changes occurring in the compound; and the ionisation side of the problem is a secondary one which only comes into play when the preliminary chemical factors are present. The colour-change in an indicator is due to the influence of an electropositive metal which brings about structural change in the molecule and produces a coloured (quinonoid) grouping. As a secondary process, ions are formed; and these are coloured, not on account of the ionisation, but simply because they are engendered by a coloured salt.

Now, in order that a compound should be of practical value as an indicator, it is necessary that these intramolecular changes should be extremely rapid—they must take place with velocities comparable with those at which ionic reactions proceed. This explains why nitro-methane, for example, is useless as an indicator; for its speed of structural change is too slow to allow it to be of any practical assistance in titrations. Thus all indicators must be either pseudo-acids or pseudo-bases; but the converse is not true, since some pseudo-acids and pseudo-bases undergo rearrangement so slowly that titration with their aid would be a needlessly lengthy process.

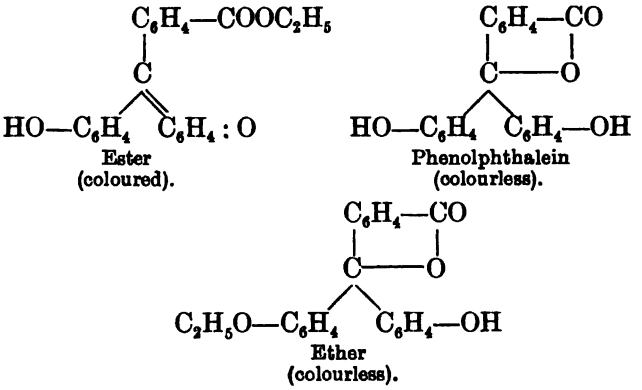
The foregoing evidence is sufficient to show that the intramolecular change theory of indicators has the weight of evidence upon its side; but in order to establish it beyond dispute, a further step was necessary. Hitherto we have been content to assume the occurrence of intramolecular rearrangement in the phenolphthalein molecule; but in order to prove the reality of this change in a conclusive manner it is necessary to isolate actual specimens of the two structural types and to show that one of them can be converted into the other. It is not necessary to use phenolphthalein itself for this purpose; a simple

* The case of anhydrous copper sulphate might be thought to conflict with this. Consideration will show, however, that before any ions are formed the material is converted into the blue pentahydrate.

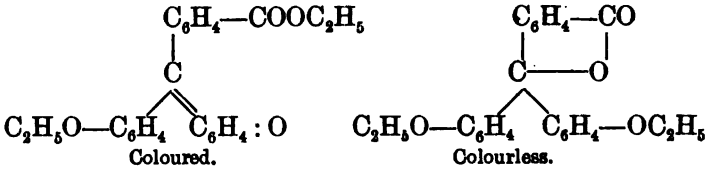
Digitized by Google

derivative will serve the purpose equally well. The evidence bearing upon the point may now be described.

Consideration of the phenolphthalein structure will show that it is possible to introduce an ethyl radicle into it in either of two ways: (1) by rupture of the lactone ring and production of an ordinary ester which must, perforce, have the quinonoid structure; or (2) by the displacement of a hydrogen atom in either of the two hydroxyl radicles, yielding a benzenoid derivative:—



The simultaneous replacement of *two* hydrogen atoms by ethyl groups will obviously give rise to two isomeric compounds having the following constitutions:—



Now when the silver salt of phenolphthalein is treated with ethyl iodide, an intensely yellow di-ethyl ester is produced[1] which is extremely labile and can be converted into a stable colourless ester even by recrystallisation. These two compounds can be represented by the above isomeric structures; and the existence of the two isomers in the solid state proves conclusively that phenolphthalein is capable of exhibiting a duplex constitution; whilst the conversion of the labile isomer into the stable

[1] R. Meyer and Marx, *Ber.*, 1907, **40**, 1414, 3603.

Digitized by Google

form shows that the intramolecular changes postulated in solution can actually be observed to take place. Thus the intramolecular change theory of the colour of indicators is placed upon a firm experimental basis.

3. *The Mechanism of Indication.*

The evidence described in the foregoing section is sufficient to prove the correctness of the intramolecular change theory of indicators; and it may be well to give here a sketch of the processes which are involved in the titration of an alkali by means of acid when phenolphthalein is used as an indicator.

In the first place, the solution of the indicator itself contains an equilibrium mixture of three things: (1) undissociated phenolphthalein in the benzenoid form; (2) undissociated phenolphthalein in the quinonoid form; and (3) the ions derived from the quinonoid form of phenolphthalein. This system we may represent by the following symbols:—

$$\underset{\text{Benzenoid.}}{HP} \rightleftharpoons \underset{\text{Quinonoid.}}{HP} \rightleftharpoons \underset{\text{Ion.}}{H^{\cdot}} + \underset{\text{Quinonoid ion.}}{P'} \quad . \quad \text{(I.)}$$

Since phenolphthalein is a very weak acid, it is feebly dissociated; and consequently the quantity of quinonoid ions in the solution is too small to render the liquid visibly coloured. The absence of colour proves also that the undissociated molecules in solution are preponderantly benzenoid in structure; so that the greatest part of the material is present as undissociated benzenoid phenolphthalein.

When the indicator is added to sodium hydroxide solution, the foregoing equilibrium is disturbed; and two processes take place which lead concurrently to the same result. One of these processes is purely ionic in nature; the other involves changes in the indicator molecule.

Taking the ionic process first, it is evident that, as the sodium hydroxide solution contains sodium and hydroxyl ions, the following interaction will occur:—

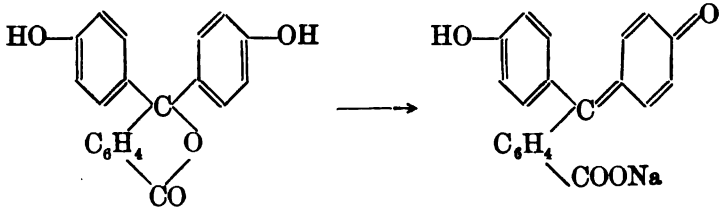
$$Na^{\cdot} + OH' + H^{\cdot} + P' = Na^{\cdot} + P' + H_2O$$

Since water is very feebly dissociated, this represents a procedure by means of which hydrogen ions are being removed from the system; and in consequence the equilibrium represented in (I.) above is disturbed. In order to re-establish

Digitized by Google

equilibrium, some of the quinonoid molecules in solution must dissociate and give rise to a fresh supply of quinonoid ions. But as has been made clear in the course of this chapter, this mechanism in itself would be unable to cause any deepening of the colour in the solution, since these quinonoid molecules are already quite as strongly coloured as the ions to which they give rise. The real origin of the increase in the colour-intensity is to be found in the next step, the conversion of benzenoid molecules into quinonoid ones in order to make up for the quinonoid molecules which have been dissociated into ions. Arguing by analogy from what is known of other equilibria among organic compounds, it seems doubtful if this purely ionic part of the mechanism represents the main process which makes indicators valuable. It appears much more probable that the second form in which the alkali operates is the really crucial factor in the indicator problem; and we must now deal with it.

In presence of alkali, the lactone ring of phenolphthalein is ruptured and the metallic salt of phenolphthalein is formed. Owing to the constitution of the compound, as has been shown earlier in this chapter, the opening of the ring necessitates the formation of the quinonoid grouping within the molecule:—



and consequently the salt is coloured. This salt then dissociates into ions, of which the anion set are quinonoid in structure and impart their tint to the solution. If, instead of sodium hydroxide, a weak base were employed, its disrupting effect upon the lactone ring would be slower and feebler than that of the powerful caustic soda; and in consequence the change from the benzenoid to the quinonoid form would be much slower and the value of the indicator in this case would be depreciated.

In the event of an acid, such as hydrochloric acid, being added to the alkaline solution of the indicator, the foregoing

Digitized by Google

processes are reversed. The hydrogen ions of the acid combine with the hydroxyl ions in the solution, forming water and leaving free together the ions of sodium and chlorine. This removal of hydroxyl ions disturbs the equilibrium of the indicator and tends to shift the equilibrium in (I.) from right to left, since the hydrogen ions from the indicator now represent a surplus in the solution. Consequently, they tend to recombine with the quinonoid ions in order to form quinonoid molecules; with the result that this section of the equilibrium is upset and a conversion of quinonoid into benzenoid molecules is produced. Again, the presence of mineral acids has been observed to produce the closing of lactonic rings; so that the addition of hydrochloric acid to the solution tends to convert the open-chain form of the indicator into the cyclic structure, thereby destroying the colour of the compound.

The foregoing considerations are sufficient to suggest certain practical points which arise in the use of indicators. Obviously if an indicator were stronger than the acid used in the titration, no colour-change could be expected at the moment of neutrality; and, again, if the salt of the indicator with the base used were subject to great hydrolysis, no accurate end-point would be detectable, since an excess of the base would be required to drive back the hydrolysis of the salt and produce colour-change in the indicator. The rules expressed in the following table, therefore, have to be observed if accuracy is to be attained:—

Solutions used		Indicator used.	Examples.
Acid.	Base.		
Strong	Strong	Any	Any.
,,	Weak	Strongly acidic . .	Methyl-orange; *p*-nitrophenol.
Weak	Strong	Weakly ,, . .	Phenolphthalein; litmus.
,,	Weak	None satisfactory .	Avoid these conditions.

Even when we are dealing with a single acid, the necessity for observing these rules makes its appearance. For example, in phosphoric acid there are three hydroxyl groups capable of acting as ionogenic centres; but these three centres have not the same ionogenic power. When phosphoric acid is titrated with a base in presence of methyl-orange, it behaves like a monobasic acid; from which it may be inferred that only one of the

Digitized by Google

hydroxyl groups is sufficiently ionised to attack the indicator. On substituting phenolphthalein for methyl-orange, the acid behaves as though it were dibasic; from which the obvious inference is that the second hydroxyl group, although unable to compete with the strongly acidic methyl-orange, is capable of a degree of dissociation sufficient to cope with the feebler acidity of phenolphthalein. The third hydroxyl group of phosphoric acid is supposed to be so weak in ionogenic power that salts formed from it are largely hydrolysed and hence no sharp end-point can be detected in its case.

4. *Conclusion.*

The mechanism of indicator action has been dealt with in some detail in the foregoing pages for more than one reason. In the first place, it furnishes a good example of the co-operation between physical chemistry and organic chemistry and shows how valuable results may be attained by the application to a single problem of types of investigation drawn from both these fields. Neither physical chemistry nor organic chemistry alone could have given us the full explanation of indicators' properties; but each science has filled in the gaps left by the other in our complete knowledge.

Secondly, it seemed advisable to deal with the matter at some length in view of the fact that in certain text-books which may fall into the hands of students, the accounts given of the chemistry of indicators are incomplete and in some cases actually misleading in a high degree. For example, the following passage may be quoted:—

"In many of these reactions" (of indicators) "**changes of structure,** *i.e.*, of valency and the arrangement of the atoms, may occur in the radical when it leaves the neutral molecule to form an ion; this does not necessarily affect the above" (Ostwaldian) "theory of indicators."[1]

Brief as it is, this passage contains several statements which might mislead a student who derived his information about indicators from it alone. In the first place, structural alterations in indicators do not take place merely in "many" cases, but in *all* cases in which colour-change is observed. Secondly,

[1] Partington, *Text-book of Inorganic Chemistry*, 1921, p. 363.

Digitized by Google

structural change and ionisation are two entirely independent phenomena, in the sense that one of them can be observed when the other is absent. It is undesirable to say that structural changes "may occur in the radical when it leaves the neutral molecule to form an ion," since it appears to be very clearly established that the structural alteration takes place in the undissociated compound, as the behaviour of esters derived from the pseudo-acids shows. Thirdly, it is surprising to find anyone maintaining at the present day that Ostwald's hypothesis is unaffected by the question of structural changes in the indicator itself. Ostwald's hypothesis is based upon the erroneous assumption that a colour-change is produced when a colourless salt or acid becomes ionised, an assumption which is in flat contradiction with all our experience up to the present. This colour-change is the very root of the question: no colour-change, no indicator; and any hypothesis which is in error in the matter of the colour-change is obviously an incorrect attempt to solve the indicator problem. It is to be hoped that, in future, misapprehensions of this kind will disappear from text-books and that something more accurate will take their place.

Digitized by Google

CHAPTER VIII.

NON-AQUEOUS IONISING SOLVENTS.

A. INTRODUCTORY.

ALTHOUGH aqueous solutions of salts are the commonest media in which electrolysis has been observed, this set of substances represents only a small group of the liquids which are capable of exhibiting marked conductivity. In 1801, Davy[1] observed that fused nitre, caustic soda and caustic potash were good conductors; and the researches of Faraday[2] extended this list very considerably. At a later date it was found that not only fused salts but also solutions of salts in non-aqueous inorganic fluids were capable of conducting the electric current; and further investigation of the field revealed that some organic solvents also possessed the same property. In the present chapter, it is not intended to deal with the conduction of fused salts; attention will be confined to the case of solutions with solvents other than water.

Two sides of the problem present themselves at once: (1) the differences and resemblances exhibited by the interaction of two salts in water on the one hand and in a non-aqueous solvent on the other; and (2) the influence which the nature of the solvent exerts upon the conducting power of the solution.

In order to illustrate these points, the present chapter will be divided into sections. In the next section, a parallel will be drawn between reactions in aqueous solution and those which take place in liquid ammonia, as this last solvent has been very fully studied in this connection. In the succeeding section of the chapter an account will be given of Walden's investigations of the relations between the chemical constitution and physical properties of the solvent on one hand and the conducting power

[1] Davy, *Journals of Royal Institution*, 1802, 33.

[2] Faraday, *Experimental Researches in Electricity*, Vol. I., p. 110, 1839.

Digitized by Google

observed when salt is dissolved in it on the other. Later sections will deal with some other relations which have been detected.

It is necessary to restrict this chapter to these two points, because a full treatment of the whole subject of non-aqueous solutions would require a volume in itself. For further information, reference may be made to various papers dealing with the matter from different points of view.[1]

B. Reactions in Liquid Ammonia.

1. *The Properties of Liquid Ammonia.*

Liquid ammonia is a colourless, mobile substance boiling at approximately − 33° C., and having a density about 0·6 that of water. At − 77° C. it solidifies to white transparent crystals.

When the properties of this body are compared with those of water, many resemblances can be traced between the two substances. The boiling-point of ammonia is considerably lower than that of water; but lies much nearer to it than do those of such substances as methane, hydrogen sulphide, or hydrochloric acid. On the other hand, the specific heat of liquid ammonia and the heat of fusion of the solid substance are greater than the corresponding constants for water and ice. The dielectric constant of liquid ammonia is about 20, which is sufficiently high to indicate that it is probably associated, like water. Its critical temperature is also comparatively high; and its critical pressure is the highest known with the exception of that of water. Its boiling-point elevation constant[2] is the

[1] Carrara, *Gazzetta*, 1903, **33**. I., 241; Centnerszwer, *Zeitsch. physikal. Chem.*, 1901, **39**, 220; Dutoit and Levier, *J. chim. phys.*, 1905, **3**, 435; Jones and Lindsay, *Amer. Chem. J.*, 1902, **28**, 329; Jones and Carroll, *ibid.*, 1904, **32**, 521; Kahlenberg *Zeitsch. physikal. Chem.*, 1903, **46**, 64; Kahlenberg and Schlundt, *J. Physical Chem.*, 1902, **6**, 447; Kahlenberg and Ruhoff, *ibid.*, 1903, **7**, 254; Mathews, *ibid.*, 1905, **9**, 641; Schlundt, *ibid.*, 1901, **5**, 157; Walden and Centnerszwer *Zeitsch. physikal. Chem.*, 1901, **39**, 513; *Zeitsch. anorgan. Chem.*, 1902, **30**, 145; Walden, *Zeitsch. physikal. Chem.*, 1900, **25**, 371; 1903, **43**, 385; **46**, 103; 1905, **54**, 129; 1906, **55**, 207, 281, 683; *Zeitsch. Elektrochem.*, 1905, **12**, 77; Baur, *ibid.*, 1906, **12**, 725; Jones, Bingham and McMaster, *Zeitsch. physikal. Chem.*, 1906, **57**, 193, 257; Jones, Lindsay and Carroll, *ibid.*, **56**, 129; Buchner, *ibid.*, **54**, 665; Steele, McIntosh and Archibald, *ibid.*, **55**, 129; Jones and Veazey, *ibid*, 1908, **61**, 641.

[2] Franklin and Kraus, *Amer. Chem. J.*, 1900, **23**, 227; **24**, 83; *J. Amer. Chem. Soc.*, 1905, **27**, 191.

Digitized by Google

lowest yet observed, being 3·4 as compared with the 5·2 of water. In the table below are some figures which serve to show to what extent the two substances resemble each other:—

	Liquid Ammonia.	Water.
Melting-point	− 77° C.	0° C.
Boiling-point	− 38·5° C.	+ 100° C.
Specific gravity at 20° C. . .	0·6284	0·9983
Critical temperature . .	+ 131°	+ 365°
Critical pressure . . .	113 atmospheres	200·5 atmospheres

Liquid ammonia has the power of dissolving many substances. Salts are not so easily soluble in it as they are in water, but on the other hand it has a much greater power of dissolving carbon compounds than water shows. Further, it is a good ionising medium; dilute solutions of substances in liquid ammonia are often better conductors than aqueous solutions of the same strength.

2. *Reactions between Inorganic Salts, Bases and Acids in Liquid Ammonia Solutions.*

The first worker to direct attention to the fact that liquid ammonia might be utilised as a solvent appears to have been Gore,[1] who, in 1872, carried out some experiments in this direction. Franklin and his co-workers[2] have dealt very fully with this problem, and we shall devote the pages immediately following to an account of the results arrived at by them.

In the first place, however, it will be convenient to give the classification of the salts which was proposed by Franklin.[2] He took as his starting-point the parallelism between water, oxygen bases and oxygen acids on the one hand, and ammonia metallic amides and acid amides on the other. The oxygenated bodies he termed hydro-salts, hydro-bases and hydro-acids; while the corresponding ammonia derivatives were named ammono-salts, ammono-bases and ammono-acids. Thus potassium nitrate is a hydro-salt; sodium hydroxide is a hydro-base; and acetic acid is a hydro-acid. Potassium acetamide, and sodium succinimide, are ammono-salts; sodamide, lead imide and mercuric nitride are ammono-bases; while acetamide, carbamide and succinimide are ammono-acids.

[1] Gore, *Proc. Roy. Soc.*, 1872, 20, 441; 1873, 21, 140.
[2] Franklin, *J. Amer. Chem. Soc.*, 1905, 27, 820.

Digitized by Google

In the present section the reactions between some hydrosalts in ammonia solution may be described; and in the later sections an account will be given of the behaviour of the ammono-class, which differs to some extent from that of the oxygen compounds.

It was shown by Franklin and Kraus[1] that when two inorganic salts are dissolved in liquid ammonia, the reaction between them may not follow the same course as it does in aqueous solution. The reason for this lies, of course, in the fact that the solubility of salts is not the same in ammonia as in water. For instance, if sodium chloride be mixed with calcium nitrate in aqueous solution, no precipitation occurs: but if the experiment be carried out in ammonia solution a precipitate of calcium chloride is obtained—a result which could not possibly be produced in aqueous solution.

As far as is known at present, metallic hydroxides are insoluble in liquid ammonia. On the other hand, when acids are brought into contact with that substance they first unite with it to give ammonium salts, which are soluble and give *acid* solutions. It should be noted that liquid ammonia is not a basic substance; so that when an acid is dissolved in it, the solution thus obtained has acid properties. This can be shown in the following way. Phenolphthalein is dissolved in liquid ammonia and is coloured by the addition of a trace of alkaline hydroxide. On adding an acid to the ammonia, the colour is discharged, though of course there is a very large excess of liquid ammonia present.

Again, just as a dilute solution of ammonium sulphate in water will dissolve magnesium, so a solution of an ammonium salt in liquid ammonia will dissolve sodium or magnesium, hydrogen being evolved in this case also. The equation of the reaction in the case of sodium and ammonium chloride is—

$$Na_2 + 2NH_4Cl = 2NaCl + 2NH_3 + H_2$$

Further, Divers had shown that such substances as sodium hydroxide were soluble in solutions of ammonium nitrate, though they are not soluble in liquid ammonia itself. Franklin[2] examined cases of ammonium salts other than the nitrate, and

[1] Franklin and Kraus, *Amer. Chem. J.*, 1899, **23**, 83.
[2] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

Digitized by Google

found that the property is a general one. It thus appears that bases dissolve in ammonia solutions of ammonium salts in a manner exactly analogous to the solution in acids of bases which are insoluble in water. Thus, as Franklin points out, the action must follow the course indicated below:—

$$NaOH + NH_4Cl = NaCl + H_2O + NH_3$$
$$CaO + 2NH_4NO_3 = Ca(NO_3)_2 + H_2O + 2NH_3$$

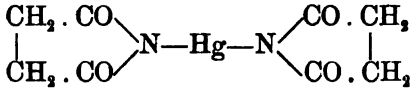
3. *The Reactions of Ammono-salts, Ammono-bases and Ammono-acids in Liquid Ammonia Solution.*

If some phenolphthalein be dissolved in liquid ammonia, it is coloured red when a metal amide is added to the solution; but the colour can be discharged by the addition of an acid amide. Thus if sodamide be allowed to react with acetamide in liquid ammonia, an ammono-salt, sodium acetamide, is formed in accordance with the following equations:—

$$CH_3 . CO . NH_2 + NaNH_2 = CH_3 . CO . NHNa + NH_3$$
$$CH_3 . CO . NH_2 + 2NaNH_2 = CH_3 . CO . NNa_2 + 2NH_3$$

These reactions have been studied by Franklin and Stafford.[1]

By analogy with the hydro-salts in aqueous solution, these ammono-salts should be good electrolytes. Franklin and Kraus[2] have tested this in the case of mercury succinimide:—



and have found it to be the case.

It will be remembered that some metallic hydroxides behave as if they were slightly acidic. For example, aluminium hydroxide dissolves in a solution of caustic potash, giving potassium aluminate. A similar class of substances has been discovered among the ammono-series; for some metallic derivatives of ammonia, such as the silver, lead and aluminium compounds, dissolve in excess of potassamide solution.

Among the ammono-bases we class such substances as metallic amides, imides or nitrides. These substances dissolve in liquid ammonia exactly in the same way as metallic hydrox-

[1] Franklin and Stafford, *Amer. Chem. J.*, 1902, **28**, 83.
[2] Franklin and Kraus, *J. Amer. Chem. Soc.*, 1905, **27**, 191.

Digitized by Google

ides dissolve in water. Potassamide is especially soluble in ammonia; and in consequence of this property Franklin [1] has utilised that substance in the preparation of a number of insoluble metallic derivatives of ammonia by simply bringing together a soluble metallic salt and potassamide in ammonia solution. The double decomposition takes place in a way perfectly analogous to that which occurs in aqueous solution, and the required body is obtained as a precipitate.

$$AgNO_3 + NH_2K = AgNH_2 + KNO_3$$
$$Pb2NO_3 + 2NH_2K = NHPb + 2KNO_3 + NH_3$$
$$3HgI_2 + 6NH_2K = N_2Hg_3 + 6KI + 4NH_3$$

The soluble metallic amides form solutions which are good electrolytes.

The ammono-acid group of substances includes a varied assortment of compounds. We have already mentioned some acid amides, and to these acid imides must be added. Further, while the nitrides of metallic elements act as bases, it has been found that the non-metallic nitrides yield acids with liquid ammonia; so that here the parallel between hydro-bodies and ammono-compounds is very close. Again, since the halogen derivatives of strongly electro-negative elements such as phosphorus are hydrolysed by water, they are attacked also by liquid ammonia, giving rise to substances analogous to the hydrolysis products, hydroxyl being replaced by the ammonia group. The following equations will make the matter clear:—

$$PCl_3 + 5NH_3 = NH:P.NH_2 + 3NH_4Cl$$
$$SiCl_4 + 8NH_3 = Si(NH_2)_4 + 4NH_4Cl$$
$$B_2S_3 + 6NH_3 = B_2(NH)_3 + 3NH_4SH$$
$$SiSBr_2 + 4NH_3 = SiS(NH_2)_2 + 2NH_4Br$$

Picramide must also be included in this category, as the ammono-analogue of picric acid:—

$HO.C_6H_2(NO_2)_3$ — Picric acid. $\qquad$ $NH_2.C_6H_2(NO_2)_3$ — Picramide.

From the foregoing, the close alliance between reactions taking place in aqueous solution and those which occur in liquid ammonia can be seen; and in order to recall this parallelism, Franklin [1] proposed the term *ammonolytic* as an analogue of

[1] Franklin, *J. Amer. Chem. Soc.*, 1905, **27**, 820.

Digitized by Google

hydrolytic. For example, when bismuth chloride is dissolved in excess of water, hydrolysis takes place and bismuth oxychloride is formed. As a parallel[1] to this, mercuric chloride, mercuric iodide and lead iodide when dissolved in liquid ammonia undergo a process of *ammonolysis*, which, like hydrolysis, is a reversible reaction:—

$$HgCl_2 + 2NH_3 \rightleftharpoons NH_2 . Hg . Cl + NH_4Cl$$
$$2HgI_2 + 4NH_3 \rightleftharpoons Hg_2N . I + 3NH_4I$$
$$2PbI_2 + 6NH_3 \rightleftharpoons (NH_2)_2Pb, NH_2 . Pb . I + 3NH_4I$$

In these cases the ammono-basic salts: $NH_2.Hg.Cl$, $Pb(NH_2)_2$; $NH_2Pb.I$ and $Hg_2N . I$ appear as solid phases, just as bismuth oxychloride is precipitated; and the solution of the oxychloride precipitate on the addition of acid here finds its parallel in the solubility of the ammono-salts in excess of ammonium salt.

C. Walden's Investigations.

1. *General.*

The following table[2] shows the influence of the chemical constitution of solvents upon the conductivity of solutions. The figures represent the values for μ_∞ at 25° C. which were obtained for solutions of triethyl-sulphonium iodide, $(C_2H_5)_3SI$.

TABLE I.

Solvent.	$\mu\infty$	*Solvent.*	$\mu\infty$
Water	107·6	*Iso*-propyl alcohol	22·0
Methyl alcohol	134·0	*Iso*-butyl alcohol	3·0
Ethyl alcohol	54·0	Benzyl alcohol	2·5
Allyl alcohol	32·0	*Iso*-amyl alcohol	2·0
n-propyl alcohol	26·0	Trimethyl carbinol	0·5

Examination of these results will reveal three points of interest. In the first place, the conductivity of triethyl-sulphonium iodide is higher in a solution of methyl alcohol than it is in water; which shows that in some cases organic solvents can yield solutions of marked conducting power. Secondly, though in general the conducting power of the solution decreases as the number of carbon atoms in the solvent molecule increases, this is not without exceptions; for benzyl alcohol contains seven carbon atoms whilst trimethyl carbinol has only four, yet the

[1] Franklin and Cady, *J. Amer. Chem. Soc.*, 1904, 26, 499.
[2] Carrara, *Gazzetta*, 1894, 24, 11, 504.

Digitized by Google

former substance yields solutions of a higher conductivity. Finally, the formation of a branched chain in a molecule appears to diminish the conducting power to some extent: normal propyl alcohol, $CH_3 . CH_2 . CH_2 . OH$, yields a solution with a conductivity four units higher than that of the isomeric *iso*-propyl alcohol in which the chain is forked, $(CH_3)_2CH . OH$; and a further forking of the chain again lowers the conducting power, as can be seen by comparing *iso*-butyl alcohol, $(CH_3)_2CH . CH_2OH$, and trimethyl carbinol, $(CH_3)_3C . OH$. Further data and references to the literature are to be found in a paper by Walden.[1] Many other classes of organic compounds had been examined before he began his work; but to him we owe the most complete investigation of the problem as a whole.

Since inorganic salts, as a general rule, are not readily soluble in organic solvents, Walden found it necessary to choose some compound which would give the required solutions and which would also dissociate into ions. An organic acid suggests itself at once to the mind; but since some of the solvents were capable of forming salts with acids, this type of reagent had to be excluded, as otherwise the results would not have been comparable throughout the series. Walden's choice finally fell upon tetra-ethyl-ammonium iodide, $(C_2H_5)_4N . I$, which was soluble in all the solvents under investigation and which would act as a normal binary electrolyte.

The selection of suitable solvents was the next consideration. In order to provide sufficient variety in chemical constitution, Walden examined about fifty compounds including alcohols, aldehydes, acids, anhydrides, acid halides, esters, amides, nitriles, thiocyanates, *iso*-thiocyanates, nitro-compounds, nitrosamines, aldoximes, ketones, sulphides and chlorohydrins.

2. *Conductivity, Dissociating Power and Dielectric Constant.*

Since the conducting power of an electrolyte is governed by the number of ions present in unit volume, by the charge carried by each ion and by the velocity with which the ions move through the solvent, it is necessary to consider the case of organic solvents in relation to these factors. In order

[1] Walden, *Zeitsch. physikal. Chem.*, 1903, **46**, 103.

Digitized by Google

to arrive at the relative number of ions present in unit volume of solution, the degree of dissociation $\left(\alpha = \frac{\lambda_v}{\lambda_\infty}\right)$ must be ascertained. With regard to the second factor, since a single electrolyte, tetra-ethyl-ammonium iodide, is utilised throughout the series of experiments, the ionic charges are constant. The velocity with which the ions traverse the solution depends upon various influences which will be considered later. For the present, attention may be concentrated upon the dissociating powers of the various solvents.

Thomson[1] and Nernst[2] pointed out that if a dissociable compound were dissolved in a solvent having a high dielectric constant it would be practically entirely dissociated, since the electrical forces uniting the atoms are thereby markedly reduced; and from this the inference may be drawn that the dissociating power of a solvent goes hand in hand with its dielectric constant. In this way the conductivities of various solutions containing the same electrolyte will be governed to some extent by the dielectric constants of the various solvents used; but since other factors besides dissociating power enter into the conductivity problem, no absolute agreement between the numerical values of conducting power and dielectric constant is to be expected: the most that can be looked for is a rough parallelism between the two properties. Further, the degree of dissociation under fixed conditions should also be connected with the value of the dielectric constant.

An examination of the figures[3] given in the following table will show that there is justification for these assumptions. In the first column are shown the conductivities at infinite dilution of tetra-ethyl-ammonium iodide in various solvents; the second column contains the degree of dissociation, α, of the salt at a dilution of 1000 litres; whilst in the third column the dielectric constants, ϵ, of the various solvents are given.

[1] J. J. Thomson, *Phil. Mag.*, 1893, **36**, 320.
[2] Nernst, *Zeitsch. physikal. Chem.*, 1894, **13**, 531.
[3] Walden, *ibid.*, 1906, **54**, 222, 139.

Digitized by Google

TABLE II.

		$\Lambda_{\infty}^{25.}$	$\alpha=\frac{\Lambda_{1000}}{\Lambda_{\infty}}$.	ϵ.
Acetic acid	CH_3COOH	21	7	6·46
Acetyl chloride	CH_3COCl	172	72	15·5
Acetone	CH_3COCH_3	225	74	21·9
Methyl *iso*-thiocyanate . .	CH_3NCS	184	77	19·7
Acetaldehyde	CH_3CHO	180	84	21·1
Methyl alcohol	CH_3OH	124	88	34·8
Methyl thiocyanate . . .	CH_3CNS	96	89	35·9
Acetonitrile	CH_3CN	200	90	36·4
Nitromethane	CH_3NO_2	120	92	40·4
Water	H_2O	—	98	81·7

It will be seen that the dielectric constants and the dissociating powers of this group of compounds fall in precisely the same order, though there is no numerical relationship between the two quantities; and this is sufficient to exhibit the influence of the dielectric constant of a liquid upon its power of decomposing a salt into ions. On the other hand, dielectric constant is evidently not a preponderant factor in the question of conducting power; for inspection will show that the order of dielectric constant and the order of conductivities are in no way connected. While the dielectric constants regularly increase as we pass down the column, the conductivities waver up and down in an irregular manner.

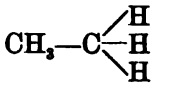
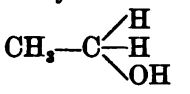
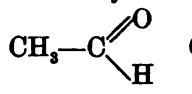
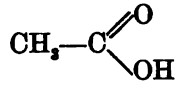
The next question which presents itself concerns the influence of the chemical character of the solvent upon the dissociating power. Walden,[1] from the results given above and others which it is unnecessary to reproduce here, deduces that the power of dissociation is conferred upon solvents by the presence of the oxygen-containing radicles: carboxyl, hydroxyl and carbonyl; by the cyanide, thiocyanate and *iso*-thiocyanate groups; and by nitro-, sulpho- and amido-groups. From an inspection of Table II., the relative influences of these various radicles can be detected; and it will be seen that the elements oxygen, nitrogen and sulphur have a marked effect upon both dielectric constant and dissociating power. In homologous series, Walden observed

[1] Walden, *Zeitsch. physikal. Chem.*, 1906, **54**, 218.

Digitized by Google

that an increase in the complexity of the hydrocarbon radicle was accompanied by a decrease in the power of dissociation.[1]

An even more interesting problem is reached when the mutual influence of two groups upon one another is considered. As can be seen from the figures below,[2] the introduction of either a hydroxyl or a carbonyl group into the ethane molecule leads to a compound of marked dissociating power; but when both carbonyl and hydroxyl radicles are introduced simultaneously, there is a very great falling off in dissociating capacity:—

Ethane.	Ethyl alcohol.	Acetaldehyde.	Acetic acid.
			
Insulator.	a_{1000} = 78 per cent.	a_{1000} = 84 per cent.	a_{1000} = 7 per cent.

This influence is so powerful that it even makes its effect noticeable in the values[3] of conductivities at infinite dilution, as can be seen from the following figures:—

		Λ_{∞}^{25}.
Ethyl alcohol	$CH_3 . CH_2 . OH$	60
Ethyl cyanide	$CH_3 . CH_2 . CN$	165
Lactonitrile	$CH_3 . CH(OH) . CN$	40

Here, although either the hydroxyl or the cyanide radicle can coexist with high conductivity, the simultaneous introduction of both groups, as in lactonitrile, leads to a lowering of the conductivity value below that exhibited by either of the simpler compounds. These results obviously recall the influences of residual affinity which were examined in Chapter II.

We must now turn to another method by means of which the degree of dissociation of a solute can be measured. Osmotic pressure is proportional to the number of particles present in a given volume of solution; and it is found that ions act as though they were individual particles in this sense. If a salt is dissociable into n ions, and if the fraction of the total

[1] See also Schlamp, *Zeitsch. physikal. Chem.*, 1894, **14**, 272, and Jones, *ibid.*, 1899, **31**, 114.

[2] Walden, *ibid.*, 1906, **54**, 155, [3] *Ibid.*, 225.

Digitized by Google

molecules present which decomposes into these ions is a, then if unit quantity of the substance be considered, the number of undissociated molecules present will be $1 - a$; and the number of ions will be na: so that the total number of particles in solution will be $1 - a + na$. This expression obviously represents the ratio between the number of particles actually present in solution and the number which would be present had no dissociation occurred; and to it van't Hoff gave the symbol i—

$$i = 1 - a + na$$

whence it is clear that

$$a = \frac{i - 1}{n - 1}$$

Now, in the case of tetra-ethyl-ammonium iodide, since it gives rise to two ions, the value of n is 2 and the expression becomes $a = i - 1$. The value of i can be obtained by comparing the calculated molecular weight in solution with that actually found in experiments; so that in this way it is possible to ascertain the degree of dissociation apart from conductivity measurements.

The determination of the molecular weight in solution can, of course, be carried out in various ways; but in the actual investigation under consideration several factors are present which restrict the choice. For example, the usual cryoscopic method is excluded owing to the fact that many of the solvents used have extremely low freezing-points. Even if the ebullioscopic method is employed, the number of solvents which can be utilised is limited by the fact that the boiling-point must not be so high as to risk a thermolytic dissociation of the tetra-ethyl-ammonium iodide into triethylamine and ethyl iodide; and a further limitation is imposed by the desirability of making the measurements at temperatures not too far removed from 25°, at which the conductivity determinations were carried out.

Confined by these restrictions, Walden[1] limited his examination to the following solvents: methyl alcohol, ethyl alcohol, acetonitrile, propionitrile, nitromethane and methyl thiocyanate.

[1] Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 281.

Digitized by Google

On comparing the values of i obtained respectively by the conductivity and the ebullioscopic method, a general agreement was found between them; but this agreement never reached absolute identity. The character of the solvent appeared to influence the deviation between the two values. In the case of the alcohols, the ebullioscopic value of i is smaller than that deduced from conductivity measurements; and the discrepancy between the two figures increases with the concentration of the solution and is greater in higher members of a homologous series than it is among the less complex ones. According to Walden, the lower value of the osmotic i is influenced by the power of association not only of the solvent but also of the solute: the greater the associating power of the solvent and the greater its mass in proportion to that of the solute, the less the solute is associated and hence the closer together the two values of i are found to lie. With the nitriles, it is found that the conductivity and boiling-point methods yield practically identical i-values; and nitromethane also gives good agreement. The most curious case is furnished by methyl thiocyanate. The conductivity results prove that the solute is highly dissociated in this solvent; but the boiling-point of the solution is actually slightly lower than that of the pure solvent—an anomaly which still awaits explanation.

3. *Conductivity and Viscosity.*

Since the conductivity of a solution depends partly upon the velocity of the ions within the liquid, it is evident that any friction encountered by these ions in their paths will affect the conducting power of the solution to an appreciable extent. Viscosity measurements allow us to gain an insight into the internal friction within a liquid; and it is therefore clear that further information upon the factors governing conductivity in organic solvents can be obtained by an investigation of the viscosities of the solvents. The following table gives some of the results.[1] In the first column the figures represent the viscosity of the pure solvents at 25° C.; and it may be noted in passing that Walden treats this value as that of an infinitely dilute solution of tetra-ethyl-ammonium

[1] Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 207.

Digitized by Google

iodide in the solvent. The second column contains the conductivities at infinite dilution of tetra-ethyl-ammonium iodide in the various solvents. The third column gives the product of the corresponding figures in the first two columns.

TABLE III.

	η_∞.	Λ_∞^{25}.	$\eta_\infty^{25} \times \Lambda^{25}$.
Acetyl chloride . . .	0·00387	172	0·666
Acetone	0·00316	225	0·711
Methyl alcohol . . .	0·00580	124	0·719
Methyl thiocyanate . .	0·00719	96	0·690
Acetonitrile	0·00346	200	0·692
Nitromethane . . .	0·00619	120	0·743
Water	0·00891	112·5	1·00

An examination of the corresponding figures in the first two columns will show that high viscosity goes hand in hand with low conductivity and *vice versâ* as theory demands. Inspection of the figures in the last column brings to light the fact that in general they approximate to 0·7; and all the results obtained by Walden in an investigation of some thirty substances point to the same value for the product of the viscosity and the conductivity at infinite dilution, provided that tetra-ethyl-ammonium iodide be used as the electrolyte throughout the series.

It seems justifiable, therefore, to assume that the expression $\eta_\infty^{25} \times \Lambda_\infty^{25} = 0{\cdot}7$ is approximately correct for this electrolyte, since it has been shown to hold good in ranges between $\Lambda_\infty = 8$ and $\Lambda_\infty = 225$. Further, if η' and η'' be the viscosities of two solvents and Λ' and Λ'' be the corresponding conductivities of the solutions which they yield with a common electrolyte, then *

$$\frac{\Lambda'}{\Lambda''} = \frac{\eta''}{\eta'}$$

Finally, the expression $\Lambda_\infty^{25} = \dfrac{0{\cdot}7}{\eta_\infty^{25}}$ allows us to calculate the viscosity of the solvent from the conductivity at infinite dilution of a solution containing tetra-ethyl-ammonium iodide as a solute.

* There appears to be a misprint in Walden's paper at this point (p. 246).

Digitized by Google

From an examination of temperature coefficients of viscosity on the one hand and of conductivity on the other, Walden deduced that these two values are practically identical for any given solvent; and this leads to the conclusion that the rule $\eta_{\infty}^{25} \times \Lambda_{\infty}^{25} = 0{\cdot}7$ is not confined to any particular temperature but will hold good throughout a range. By measurements at zero, he was able to confirm this idea.

A highly important theoretical deduction was drawn by Walden from these results. According to previous hypotheses, as was mentioned above, ionic velocity was assumed to be dependent upon ionic friction. Walden's results show, however, that for each solvent there is a characteristic ionic velocity—*i.e.*, that the governing factor is the nature of the *solvent*. This suggests that the only friction concerned in ionic migrations is a friction between solvent molecules. As Walden points out, this implies that each solute ion is surrounded by a coating of solvent molecules and that the whole associated complex suffers a friction which is practically indistinguishable from that which exists between particles of the solvent alone.

4. *Solvent Power and Heat of Solution.*

In pursuance of his plan, Walden[1] next examined the solvent power of the various liquids with which he had previously dealt, measuring solvent power by the solubility of tetra-ethyl-ammonium iodide in the solvent under consideration.

As was to be expected, the solubilities observed varied greatly among themselves, running from 35·5 to 0·0004 parts by weight of solute per 100 c.c. of solvent. In every case, the temperature coefficient of solubility was positive, *i.e.*, the solubility increased with rise in temperature; and in the case of solvents containing hydroxyl groups, which are most associated, the temperature coefficients were greatest. Between the association factor for the solvent and the solubility of tetra-ethyl-ammonium iodide, only a purely qualitative relation could be traced; though, as might have been anticipated, the solute dissolved most readily in the solvents with highest association constants. Since the formation of ions increases the solubility of a salt, it might have been predicted that solvents with high

[1] Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 683.

Digitized by Google

dielectric constant—and therefore great ionising power—would yield the most concentrated solutions; and as a general rule this appeared to be the case, though there are certain exceptions to it in the case of solvents capable of tautomeric change.

When the problem of the degree of dissociation of a single solute dissolved in various media is examined, Walden's results [1] lead to a deduction of great theoretical and practical importance.

He found that in practically every case examined by him, solutions saturated with tetra-ethyl-ammonium iodide at 25° C. had the same degree of dissociation :—

$$a_1 = a_2 = a_3 = 0{\cdot}48$$

In other words, for the given electrolyte the point of saturation is reached in each solvent when each of the solutions has the same degree of dissociation.

Expressing this in symbolical form :—

$$\frac{\Lambda'}{\Lambda'_\infty} = \frac{\Lambda''}{\Lambda''_\infty} = a' = a''$$

whence $$\frac{\Lambda'}{\Lambda''} = \frac{\Lambda'_\infty}{\Lambda''_\infty} \text{ or } \Lambda' = \frac{\Lambda''\Lambda'_\infty}{\Lambda''_\infty}$$

or, restating the matter in other words: the molecular conductivities Λ' and Λ'' of two saturated solutions of the same electrolyte in different solvents are in the ratio of the values of the limiting conductivities Λ'_∞ and Λ'_∞.

Now, in the case of tetra-ethyl-ammonium iodide, it has already been established that $\Lambda'_\infty \eta'_\infty = \Lambda''_\infty \eta''_\infty = 0{\cdot}7$, so that

$$\frac{\Lambda'}{\Lambda''} = \frac{\Lambda'_\infty}{\Lambda''_\infty} = \frac{\eta''_\infty}{\eta'_\infty}$$

from which it is obvious that the molecular conductivities of two saturated solutions of the same electrolyte are inversely proportional to the viscosities of the pure solvents.

The practical bearing of this lies in the fact that we are now able to calculate the molecular conductivity of a saturated solution of an electrolyte in a solvent A, provided that we know the conductivity of the electrolyte in a saturated solution

[1] Walden, *Zeitsch. physikal. Chem.*, 1906, 55, 706.

Digitized by Google

of solvent B, as well as the viscosities of the two solvents, since this leaves only one unknown in the equation:—

$$\Lambda' = \frac{\Lambda'' \eta''_\infty}{\eta'_\infty}$$

In order to test the value of this method, Walden calculated a number of conductivities and compared the results with the actual experimental figures. In a series of ten cases,[1] the highest deviation was about 5 per cent., which seems a remarkable agreement.

From the foregoing evidence, it is clear that there is in some respects a close parallelism between water and many organic solvents; and it is natural to inquire whether any further resemblances can be detected. The phenomena of heats of solution suggest themselves for investigation; and it was to them that Walden[2] next turned his attention.

It may be recalled that in the case of a non-dissociated solute, if C be the concentration, T the absolute temperature, R the gas constant and q the heat of solution, the following expression holds good:—

$$\frac{d \log C}{dT} = \frac{q}{RT^2}$$

In order to make this applicable to electrolytes, it is necessary to introduce into it van't Hoff's factor i, so that it becomes—

$$\frac{d \log iC}{dT} = \frac{q}{iRT^2}$$

The correctness of this equation has been demonstrated practically by Noyes and Sammet[3] in the case of inorganic salts dissolved in water; and Walden proceeded to apply it to the case of the iodides of tetra-ethyl- and tetra-propyl-ammonium iodide in organic solvents.

The results obtained by him proved that van't Hoff's equation applied equally well to organic solvents; which establishes a further parallelism between aqueous and non-aqueous ionising media. Further, Walden showed that when

[1] Walden, *Zeitsch. physikal. Chem.*, 1906, **55**, 708.
[2] *Ibid.*, 1907, **58**, 479; **59**, 192.
[3] Noyes and Sammet, *ibid*, 1908, **48**, 513.

Digitized by Google

a solute absorbs heat in the process of solution its solubility increases with rise in temperature: a result which was to be expected from Le Chatelier's theorem.[1]

5. *Refractivity and Molecular Solution Volume.*

In the hope of detecting a relationship between the molecular refraction and the degree of dissociation of a salt when dissolved in an organic solvent, Walden[2] examined numerous solutions of tetra-ethyl-ammonium iodide. Since the iodine ion has a refractive power of 16·6 whilst the refractivity of the un-ionised iodine atom is only 14·12, it was to be expected that two results might be looked for. In the first place increase in dissociation should produce greater refractive power in the salt; so that when several solutions in the same solvent but with different dilutions are investigated, it might be anticipated that there would be a steady rise in the refractivity of the solute as the dilution increased, owing to the greater ionisation occurring in dilute solutions. Secondly, comparison between two solutions of the same strength might have been expected to bring out differences in refractive power; for the solvent with the greater dissociating power should confer higher refractivity upon the solute, since a greater number of ions will be formed in the solution.

The actual experiments showed that these expectations were not fulfilled. Instead of an increase in the refractive power of the iodide on dilution, there was, in the majority of cases, an actual diminution of molecular refraction on passing from the concentrated to the dilute solutions. The second factor in the problem also failed to give the expected results, for whether the dissociating power of the solvent be gauged by the conductivity results or by the dielectric constant, there is no parallelism between it and the molecular refractive power of the solute. The following table will serve to give some idea of the type of differences which were observed:—

[1] Le Chatelier, *Compt. rend.*, 1885, **100**, 50, 441.
[2] Walden, *Zeitsch. physikal. Chem.*, 1907, **59**, 385.

Digitized by Google

TABLE IV.

	V.	$[R_L]$.	α.	ϵ.
Methyl alcohol	3·21	58·98	0·836	34·8
	12·86	58·52	0·525	
Methyl thiocyanate	6·04	61·55	0·485	35·9
	25·00	61·42	0·66	
Acetonitrile	8·57	60·34	0·496	36·4
	17·14	59·80	0·559	
Nitromethane	5·14	59·91	0·472	40·4
	10·28	59·85	0·552	
Water	5·14	58·88	0·638	81·7
	10·28	58·85	0·724	

Here V represents the volume of solvent, $[R_L]$ is the molecular refraction of the solute calculated according to the Lorenz-Lorentz formula, α is the degree of dissociation ascertained from conductivity measurements, and ϵ is the dielectric constant of the solvent.

Examination of the figures will show that there is little or no change in the molecular refractivity with change of dilution; but that when the solvent is varied while all other conditions are kept constant, there is a marked alteration in refractive power. For example, at a dilution V = 5·14, there is a whole unit of difference between the refractivities in nitromethane and in water.

Since Walden was endeavouring to throw light upon the behaviour of organic solvents from as many points as possible, it was natural that he should endeavour to discover some other property which varied in parallel with the molecular refractivity of the solute. In other words, he began to seek for some solute property which varies but slightly on dilution but which is markedly influenced by alteration in the solvent. This property he found in molecular solution volume; and it may be well to make the meaning of this term clear before proceeding further.

When a solute is dissolved in a solvent, a change of total volume often occurs, so that the bulk of the solution is either greater or less than the sum of the separate bulks of solvent and solute before mixing took place. This change in volume is probably made up of two factors, one depending on the alteration in the bulk of the solvent and the other on the

Digitized by Google

change in that of the solute; since solvent and solute must be supposed to affect each other reciprocally. But under these conditions calculation would be impossible; and it is usual to assume that the change in volume occurs mainly in the solute and that the alteration in bulk of the solvent is negligible. In practice, this assumption is found to open the way to the fairly accurate calculation of the change of volume when solute and solvent are mixed; so that, although strictly speaking incorrect, it is a good working hypothesis.

Now let d be the density of the solution; d_o the density of the solvent; M the molecular weight of the solute; m the number of molecules of the solute present in a litre of solution; V the number of litres in which one gramme molecule of the solute is dissolved; and ϕ the molecular volume of the solute before dissolution. (It is evident that $m = 1/\mathrm{V}$.)

Take the case of one litre of solution for consideration. Before mixing took place, it is evident that there must have been present $m\phi$ c.c. of solute and $\frac{1000d - m\mathrm{M}}{d_o}$ c.c. of solvent; and since the final volume of the solution after mixing is 1000 c.c., it is obvious that the total contraction due to mixing is represented by—

$$(m\phi - m\psi) = \left(\frac{1000d - m\mathrm{M}}{d_o} + m\phi - 1000\right) \text{c.c.}$$

where $m\phi$ is the volume of the solute before the solution and $m\psi$ is its volume after solution has taken place—*i.e.*, the molecular solution volume of the solute under the conditions of experiment.

Rearranging the equation and substituting 1/V for m, we obtain the following:—

$$\psi = \frac{\mathrm{M}}{d_o} - 1000\mathrm{V}\left(\frac{d - d_o}{d_o}\right)$$

which provides a form of expression convenient for application in practice since all the factors are readily measureable.

On determining the molecular solution volumes of tetraethyl-ammonium iodide at various dilutions in different solvents, Walden observed that in the same solvent, dilution had but little influence upon the volume of the solute. Thus when

Digitized by Google

one gramme molecule of tetra-ethyl-ammonium iodide is dissolved in 5·142 litres of nitromethane the molecular solution volume is 174·39 c.c., whilst in 20·570 litres it is 172·3 c.c. On the other hand, the substitution of one solvent for another produces a marked change in the molecular solution volume; for at the same concentration (V = 5·142) the values in water and in nitromethane are respectively 186·32 and 174·39. The following table gives some of the results observed by Walden:—

TABLE V.

		V.	$[R_L]$.	ψ.
Acetonitrile . . .	CH_3CN	8·570	60·34	161·00
Methyl thiocyanate . .	CH_3CNS	6·041	61·55	169·09
Nitromethane . . .	CH_3NO_2	5·142	59·91	174·39
Glycol	$HOCH_2CH_2OH$	6·427	58·57	180·69
Water	H_2O	5·142	58·88	186·82

From these figures it will be seen that the molecular refractivity of the solute, $[R_L]$, varies inversely as the molecular solution volume, ψ; though there is no direct numerical relation between the two values.

Walden also calculated the co-volumes of the pure solvents and found that, in general, the solute's molecular refractivity increases with the co-volume of the solvent; but as there is uncertainty about the exact values of some co-volumes, it is unnecessary to give examples of this relation here.

6. *Electrostriction.*

In his next series of investigations, Walden[1] was drawn into a further examination of volume relations; but before dealing with his results it will be best to give a short account of the phenomena observed in aqueous solutions, in order to provide a standard of comparison.

As has been seen in the last section, molecular volume and molecular solution volume are not interchangeable terms; for when a substance is dissolved in a solvent, its volume generally suffers a contraction, so that the molecular solution volume is less than the ordinary molecular volume which it occupies in

[1] Walden, *Zeitsch. physikal. Chem.*, 1907, **60**, 101.

Digitized by Google

the pure state. Working mainly with aqueous solutions Traube[1] found (1) that molecular volume is an additive property—*i.e.*, it can be calculated by summation of the volume constants of the various atoms in the molecule; (2) that with increase of dilution there is a diminution of molecular volume; and (3) that under fixed conditions of temperature, all ions have the same effect on molecular volume; and (4) that in different solvents this influence varies directly with the dissociating power of the solvent.

In order to account for these phenomena, Traube assumed that they were due to osmotic pressure; Drude and Nernst,[2] on the other hand, preferred to regard the contraction as being caused by the electrostatic fields produced by the presence of ions in the solution; and they therefore christened the phenomenon *electrostriction*.

When the molecular solution volume of a feeble, non-ionised acid is compared at 15° C. with the volume of its completely ionised sodium salt, a contraction 15 c.c. is observed in passing from the acid to the salt. Now the contraction due to the replacement of hydrogen by sodium is found experimentally to be 1·5 c.c., so there remains to be accounted for a contraction of 13·5 c.c. Since this value, 13·5 c.c., is always obtained no matter what binary electrolyte is employed, it seems clear that it is attributable to the dissociation of the electrolyte into its ions and not to any specific characteristic of the electrolyte itself.

In order to calculate the electrostriction (molecular contraction) of a completely dissociated electrolyte in a given solvent, it is necessary to ascertain the molecular solution volume and the degree of dissociation of the solute at two different concentrations in this solvent and then apply the following formula:—

$$\text{Molecular contraction} = \frac{\psi_1 - \psi_2}{a_2 - a_1}$$

For example, in methyl alcoholic solution, tetra-ethyl-ammonium iodide yields these results:—

[1] Traube, *Ber.*, 1892, **25**, 2989; 1894, **27**, 3177; *Zeitsch. anorgan. Chem.*, 1893, **3**, 11; 1895, **8**, 59; and Traube, *Ueber den Raum von Atome*, 1899.

[2] Drude and Nernst, *Zeitsch. physikal. Chem.*, 1894, **15**, 79.

Digitized by Google

One gr. mol. salt in	ψ.	$\alpha = \frac{\Lambda v}{\Lambda_\infty}$.
2·475 litres	167·3	0·356
50·000 ,,	162·8	0·665

Whence $$\frac{\psi_1 - \psi_2}{a_2 - a_1} = \frac{167{\cdot}3 - 162{\cdot}8}{0{\cdot}665 - 0{\cdot}356} = 14{\cdot}6$$

By calculating in this manner, the following results are obtained :—

TABLE VI.

	Electro-striction.
Methyl alcohol	14·6
Nitromethane	12·8
Acetonitrile	10·7
Propionitrile	14·9
Methyl thiocyanate	12·5
Glycol	12·0

Bearing in mind the errors which may creep into the measurements of density and conductivity, the deviations of these figures from a mean value 13·00 are not remarkable; and Walden concluded that the electrostriction (molecular contraction) for the given electrolyte, tetra-ethyl-ammonium iodide, is in general independent of the nature of the solvent medium and is approximately 13·00 c.c. at 25° C.

This value 13·00 is, however, practically the same as that found by Traube (12·5 – 13·5 c.c.) in the case of aqueous solutions of binary electrolytes; so that here again there is a close parallelism in the behaviours of aqueous and non-aqueous solvents.

7. *Solvent Power and Dielectric Constant.*

In a previous section, the influence of a high dielectric constant in a solvent upon that solvent's dissociating power was touched upon; but the matter may now be considered in more detail from a different point of view. If the equilibrium between a solid salt, its undissociated molecules in solution and the ions into which it breaks up be represented thus :—

$$\text{Solid salt} \rightleftharpoons \text{Dissolved molecules} \rightleftharpoons \text{Ions}$$

it is evident that any influence tending to increase the number of ions in solution will conduce to the dissolution of more solid salt. Thus if a single electrolyte be dissolved in two solvents of different dielectric constant, the probability is (leaving all

Digitized by Google

other factors out of consideration) that the electrolyte will show greater solubility in the solvent having the higher dielectric constant.

It is of interest to discover whether this influence of the dielectric constant is a predominating one or whether it is masked by other factors in the problem. Walden [1] has supplied certain data which allow us to come to a conclusion on the point.

The problem is by no means so simple as it appears at first sight; for when we speak of "dielectric constant" it must be remembered that for the sake of strict accuracy the wave-length of the electrical vibrations ought to be given, just as in the case of refractive index it is necessary to mention the wave-length of light which was employed in the measurements. Again, just as molecular refractivity varies with temperature, so the results of dielectric constant determinations depend to some extent upon the temperature at which they are carried out. Finally, the electrical spectrum of a certain class of substances —hydroxyl derivatives—exhibits "anomalous electrical absorption" in a manner parallel to the selective light-absorbing power shown by coloured materials. All these factors make it difficult to find a satisfactory value for this "constant". Despite these difficulties, however, Walden was able to detect a most curious relation between solvent power and the dielectric constant, a relationship which appears to be perfectly general, since the solvents examined by him vary widely in chemical character from one another.

In Table VII., the first column of figures represents the solubilities of tetra-ethyl-ammonium iodide in various solvents, the values being expressed in molecular percentages. The second column contains the various wave-lengths of the electrical vibrations used in determining the dielectric constant, expressed in centimetres; and the sign ∞ is employed to represent waves of infinite length. The third column gives the value of ϵ, the dielectric constant deduced from observations with this wave-length. The last column contains the value of the expression $\epsilon S^{-\frac{1}{4}}$ or, where two sets of figures are given for ϵ, the mean of the $\epsilon S^{-\frac{1}{4}}$ value derived from them. The symbol S represents solubility.

[1] Walden, *Zeitsch. physikal. Chem.*, 1908, **61**, 633.

Digitized by Google

TABLE VII.

	S.	Wave-length.	ϵ.	$\frac{\epsilon}{\sqrt[3]{S}}$
Bromobenzene .	0·00369	75	5·3	50·5
		∞	9·8	
Acetone . . .	0·0718	73	20·7	51·2
		1200	21·85	
Benzonitrile . .	0·1813	75	26·0	45·9
Propionitrile . .	0·2136	75	27·2	45·5
Acetonitrile . .	0·6175	84	36·4	42·8
Nitromethane .	1·163	84	40·4	46·0
		1200	53·36	
Water . . .	3·318	1200	73·92	50·5
		∞	77·95	

Examination of these figures brings out at once the close parallelism between the solubility and the dielectric constant; the low solubility of the iodide in bromobenzene (0·00369) finds its parallel in the low dielectric constant (5·3 – 9·8); whilst at the other end of the series lies water with a solvent power a thousand times as great (3·318) and a high dielectric constant (74-78).

When a comparison is made between the dielectric constant and the cube root of the solubility, an even more direct connection between the two can be deduced. The figures in the last column represent the ratio $\sqrt[3]{S} : \epsilon$; and it will be seen that they all approximate closely to a mean value of 48. Thus if ϵ and ϵ' be the dielectric constants of two solvents and S and S′ be their solvent powers, the following expression holds good with a very fair degree of approximation:—

$$\frac{\epsilon}{\epsilon'} = \frac{\sqrt[3]{S}}{\sqrt[3]{S'}} = \text{constant (approx. 48)}$$

When it is remembered that for the thirteen solvents described by Walden the solvent power varies between values standing to one another in the ratio of 1 : 1000; and when in addition the uncertainties attending upon the evaluation of the dielectric constant are borne in mind; it must be admitted that the agreement among the figures in the final column is much closer than could be expected from any purely fortuitous result.

Digitized by Google

D. Some other Relationships.

1. *Abnormal Cases.*

In previous sections of this chapter, many resemblances between water and other liquids have been described; but any account of the subject would be incomplete if attention were not drawn to sundry divergences from the normal which have been observed in the case of non-aqueous solvents.

It has been pointed out above that, in general, solutions of electrolytes in organic solvents behave like aqueous solutions, in that their molecular conductivities increase with dilution. An exception to this rule is found, however, in the cases of ethyl ether, $(C_2H_5)_2O$, and *iso*-amyl alcohol, $(CH_3)_2CH \cdot CH_2CH_2OH$; for when hydrochloric acid is dissolved in either of these, the solution diminishes in molecular conductivity either on dilution or when the temperature is raised.[1] The same type of abnormality on dilution is found in solutions of electrolytes dissolved in liquid hydrochloric, hydrobromic and hydriodic acids and also when the solvent is liquid hydrogen sulphide, as Archibald and McIntosh have observed. Here, as in the case of liquid ammonia, the liquefied gas shows very feeble conductivity until an electrolyte is dissolved in it.

The employment of inorganic liquids as solvents for electrolytes was investigated by Walden.[2] He observed that the dissociating power of the solvent depends upon its chemical character, as the following list shows:—

Strongly dissociating	SO_2	$POCl_3$	$SbCl_3$	$AsCl_3$	SCl_2
Weakly ,,	SO_3	PCl_3	$SbCl_5$	$SiCl_4$	Br

It will be seen from the above data that there is no direct connection between the valency exerted by the main atom in the compound and the dissociating power, since on the one hand trivalent antimony is a better dissociator than quinquevalent antimony; but on the other hand quinquevalent phosphorus has a greater dissociating power than trivalent phosphorus. Nor has the introduction of an extra atom of oxygen any predictable influence, since the passage from SO_2 to SO_3

[1] Kablukoff, *Zeitsch. physikal. Chem.*, 1889, **4**, 431-2.

[2] Walden, *Zeitsch. anorgan. Chem.*, 1900, **25**, 209; 1902, **29**, 371; *Zeitsch. physikal. Chem.*, 1902, **39**, 217.

Digitized by Google

corresponds to a decrease in dissociating capacity whilst the contrary is found in passing from PCl_3 to $POCl_3$.

In connection with these inorganic solvents, another point[1] may be mentioned, which is certainly striking. In the case of conducting solutions it is normally necessary to use as a solute some compound which is acidic, basic or salt-like in its character; for substances such as sugar, which belongs to none of these classes, do not conduct the current when dissolved in water. When, however, tin, sulphur, phosphorus, arsenic, antimony, chlorine, bromine or iodine are dissolved in solvents such as liquid sulphur dioxide or arsenic trichloride it is found that the solutions have a marked conductivity. If it be assumed, as usual, that only ions can carry the current, then what ions can be expected from the dissociation of a chlorine molecule, unless it be postulated that chlorine is made up of positive and negative atoms?[2] But if this postulate were granted, it is difficult to see why all the chlorine in sodium chloride appears at the anode on electrolysis. Walden terms "abnormal electrolytes," the substances shown by him, to have this peculiarity.

In connection with the influence of chemical character upon dissociating power, a curious point comes to light when the following solvents are considered:—

Hydrocyanic acid	H.CN	H.OH	Water
Cyanogen	NC.CN	HO.OH	Hydrogen peroxide

Liquid hydrocyanic acid is found to have a greater dissociating power than water itself*; but when the hydrogen atom is replaced by the —CN radicle to form cyanogen, the latter is found to have only feeble[3] dissociating powers. On the other hand, when the hydrogen atom of water is replaced by a hydroxyl radicle to produce hydrogen peroxide† there is an increase in dissociating power.[4] The abnormality of these results will be apparent if it be remembered that both —OH and —CN groups act as anions when ionised; so that their electrical characters are similar; and yet in this case they produce opposed effects.

[1] Walden, *Zeitsch. physikal. Chem.*, 1903, **43**, 385.

[2] Compare J. J. Thomson's work on hydrogen (*Nature*, 1895, **52**, 451).

[3] Centnerszwer, *Zeitsch. physikal. Chem.*, 1902, **39**, 217.

[4] Jones, Barnes and Hyde, *Amer. Chem. J.*, 1902, **27**, 22.

* Its dielectric constant, 95, is also higher than that of water, 81·7.

† Here also the dielectric constant is increased by the substitution, for the value for water is 81·7 while that of hydrogen peroxide is 93.

Digitized by Google

2. *Mixed Solvents.*

Hitherto in this chapter attention has been confined to the cases in which the solvents were homogeneous materials; but before concluding, it will be advisable to deal briefly with some examples wherein an electrolyte is dissolved in a mixture of two miscible fluids; for under these circumstances certain phenomena have been observed which throw light upon the processes in operation in solutions. Before entering upon concrete cases, however, it will be best to deal with certain governing factors in the problem.

The researches of Dutoit and Aston [1] showed that a connection can be traced between the dissociating power of a solvent and the degree in which the solvent molecules are associated into complexes. The relation between molecular association and dissociating power is not a rigid one; but it is present in a number of cases sufficient to make it worth taking into account in any interpretation of conductivity phenomena. The assumption is made that if a liquid has the power of gathering together its own molecules into large complex groups it will have, at the same time, the power of attracting to these groups the ions of a solute; and that this process of attraction will result in the decomposition of the solute molecule into ions. On these premises, therefore, it is necessary to consider the dissociation of an electrolyte as consisting of two processes: (1) the break-up of the electrolyte's molecule into ions; and (2) the attachment of these ions to large complexes of solvent molecules.

Now suppose that a second solvent be introduced, which is also capable of a high degree of association. It is evident that it also will tend to form molecular complexes; but, further, that there will be a competition between the two solvents. For if Solvent I. be capable of tearing down molecules to form ions, it will be equally capable of tearing apart the complexes of Solvent II.

The influence of these hypothetical processes upon the conductivity of a solution thus produced would obviously be twofold. In the first place, since the two solvents are mutually engaged in destroying each other's complexes, the solvent

[1] Dutoit and Aston, *Compt. rend.*, 1897, **125**, 240.

Digitized by Google

mixture as a whole will show less molecular complexity than either solvent separately; and hence it will have less dissociating power: so that the net result will be the formation of fewer ions in the solution than would be produced in either of the pure solvents. Secondly, since the solvent complexes in the mixed solution are smaller than those in the pure solvents, and since it was assumed that each ion was associated with a complex, it is evident that the ions in the mixed solvents will be less impeded in their movements by friction within the solution than would be the case in either of the pure solvents. Thus, compared with solutions in pure solvents, the electrolyte in the mixed solvents would give rise to fewer ions; but these ions would have greater mobility than they would display in the pure solvents. Thus in the mixture there are two forces acting against one another: one tending to decrease the conductivity owing to a paucity of ions, the other increasing the conductivity owing to the increase in the velocity of ionic migration.

The foregoing statement of the case is purely hypothetical; and in order to test the validity of the hypothesis it will be necessary to turn to the experimental data which have been accumulated in this region of the subject.

The first work in this field appears to have dated from the observation[1] that the conductivities of certain salts in a mixture of methyl alcohol and water were lower than comparable conductivities in either pure water or in pure methyl alcohol. An extension of this work to include ethyl and propyl alcohol as well as mixtures of the four solvents with each other[2] proved that the same abnormality was present in these cases also.

These facts are in agreement with the hypothesis outlined above; but they are not sufficient to prove it. In order to do that, it is necessary to establish definitely that the addition of one solvent to another does actually disintegrate the molecular complexes in the liquids. Evidence on this point was obtained by Murray.[3] Working with water, formic acid and acetic acid, all of which are known to be associated, he determined the molecular weight of each of these liquids when dissolved in one

[1] Zelinsky and Krapiwin, *Zeitsch. physikal. Chem.*, 1896, **21**, 35.
[2] Lindsay, *Amer. Chem. J.*, 1902, **28**, 329.
[3] Murray, *ibid.*, 1903, **30**, 198.

Digitized by Google

of the other pair; and his observations showed that the molecular weights became smaller with increase in dilution of the solutions used. From this, the deduction may be drawn that the action of the solvent—which becomes more powerful as dilution increases—is to break up the molecular complexes formed by the solute molecules among themselves.

We have still to deal with the second part of the hypothesis: the effect of internal friction in the pure solvents and in the mixture. This was investigated by Carroll[1] by comparing the viscosities of a series of mixtures with the conductivities of solutions prepared from these mixtures. The conductivity curves and the curves of viscosity were found to be very similar; and minima occurred at corresponding points on each curve.

The existence of two opposing forces in the solutions is brought out by the behaviour of cobalt chloride dissolved in certain mixtures of acetone and the alcohols.[2] These solutions exhibited negative temperature coefficients in their conductivities; which is accounted for on the above hypothesis by assuming that although with rise in temperature the viscosity of the medium is decreased and the conductivity therefore tends to increase, yet at the same time the molecular complexes in the solution are so much simplified by the rise in temperature that the dissociating power of the solvents falls to an extent which outweighs the effect of the increased velocity of ionic migration.

It will be seen that the experimental results appear to be quite in agreement with the hypothesis suggested at the beginning of this section; so that it probably contains a good deal of truth.

[1] Carroll, *Amer. Chem. J.*, 1904, **32**, 521.
[2] McMaster, *ibid.*, 1906, **36**, 325.

Digitized by Google

CHAPTER IX.

COLLOIDS.

1. *General.*

WHEN a solid is mixed with a liquid, the system may assume one of three forms. In the first place, the particles of the solid may be large. In this case, though the mixture is apparently homogeneous after shaking, it soon separates into two layers owing to the massive particles of solid sinking to the bottom, leaving a clear liquid above them. Such a system is termed *a suspension*. Secondly, the solid particles may be extremely fine. If their size be sufficiently small, it is found that even on long standing the mixture apparently remains homogeneous; no solid separates from the liquid, and the system possesses certain peculiar properties of its own. This represents *a colloidal solution*. Finally, when the solid is distributed through the liquid in particles of molecular magnitude, *a true solution* is formed.

From the foregoing, it is easy to see that no sharp lines of division can be drawn between the three classes, since each merges into the other by imperceptible degrees. If the solid particles of a suspension be imagined as steadily diminishing in size, they are sure, sooner or later, to attain a diameter sufficiently small to permit them to float indefinitely in the surrounding liquid; and in practice it is impossible to define exactly the size of particle which will fulfil this condition. Thus a fine-grained suspension merges by imperceptible degrees into the colloidal state.

The colloid in its turn, by an analogous process of subdivision, may be conceived as passing into the form of a true solution; for if the suspended particles be decreased in size until each of them contains at most only a few molecules, the difference between colloid and true solution will be practically negligible from this point of view.

Digitized by Google

Although only very rough estimates are possible, owing to this shading of one class into another, the following figures give some idea of the relative sizes of the particles in the three different groups. In what may be termed a coarse suspension, the diameter of the particles rises from a minimum of $0{\cdot}1\mu$.* Colloidal solutions contain particles ranging between $0{\cdot}1\mu$ and $1{\cdot}0\mu\mu$; whilst true solutions contain particles with diameters of $1{\cdot}0\mu\mu$ or less.

From what has been said above, it is evident that when a material is termed colloidal in character the name indicates a *state of matter* and is not used to describe a particular chemical class of substances.

In order to bring out the meaning of various terms employed in dealing with colloidal substances, it will be best to take up the subject more or less in chronological order and to begin with the initial researches of Graham.[1] In the course of his investigations upon diffusion, Graham was led to draw a distinction between two classes of materials. Sodium hydroxide, potassium sulphate, sugar and magnesium sulphate all show a high power of diffusion in solution; whereas silicic acid, aluminium hydroxide, starch, tannin, albumin and gelatine were marked out by the low velocity with which they diffuse through water. Since crystalline compounds are rapidly diffusible whilst those showing low rates of diffusion are amorphous in character, Graham termed the first group *crystalloids* and gave the name *colloids* (from κόλλα = glue) to the latter. He suggested that the colloidal condition is a "dynamical" state of matter as opposed to the "statical" nature of the crystalloids.†

This difference in diffusive power suggested to Graham a method of separating crystalloids from colloids by means of a membrane of vegetable parchment, through which the crystalloids are able to pass rapidly whilst the colloids, owing to their low rate of diffusion, are retained behind. This process he termed *dialysis;* and the cylinder closed at one end with

[1] Graham, *Phil. Trans.*, 1861, **151**, 183; *Proc. Roy. Soc.*, 1863, **13**, 335.

* $1\mu = 10^{-3}$ mm. and $1\mu\mu = 10^{-6}$ mm. The unit 1μ is termed a *micron*.

† There is no sharp chemical division between colloids and crystalloids. Sodium chloride can be obtained in the colloidal state and some albumins can be crystallised under certain conditions.

Digitized by Google

a parchment drum, which is usually employed for this purpose, is named a dialyser. A complete separation of colloid from crystalloid is not attainable by dialysis, probably; but certainly in practice it is possible to reduce the quantity of crystalloid to such an extent that the remaining fraction is less than can be detected by ordinary analytical processes.

At this point it may be advantageous to introduce a concrete example to illustrate the use of further terminology. When a solution of sodium silicate is poured into a large excess of dilute hydrochloric acid, no precipitate of silicic acid is formed. After dialysis, it is found that all the hydrochloric acid has vanished from within the dialyser, whilst the greater part of the silicic acid remains behind in solution. On the other hand, if the process be reversed, the hydrochloric acid being added gradually to a solution of sodium silicate, a gelatinous precipitate of silicic acid is produced.

It is thus clear that silicic acid can exist in two different forms, one of which remains in the liquid in which it is produced, whilst the other is immediately thrown out of solution, in the shape of a jelly. To distinguish between these two types, Graham gave the name *sol* to the former and christened the gelatinous precipitate a *gel*. The process by which a sol is converted into a gel was named pectisation or, to use the word more commonly employed nowadays, *coagulation*.

Finding that solvents other than water could be used, Graham drew a further distinction in nomenclature by associating the words sol and gel with prefixes which represent the nature of the solvent. Thus when water was used, he spoke of hydrosols and hydrogels; with alcohol, the terms alcosols and alcogels were used; glycerine gave rise to the names glycerosols and glycerogels.

The investigation of the properties of colloid sols proves that they are divisible roughly into two classes. In the one class are placed those which have a viscosity differing but little from that of the pure solvent; and to these sols the name *suspensoids* is given. The members of the second class show a highly viscous character, being quite different in this respect from the pure solvent; and they are named *emulsoids*.

When certain sols are evaporated to dryness and pure solvent is then poured upon the residual solid it is found that the

Digitized by Google

solid again passes into the sol condition in the fluid. In this case, the material is said to be *lyophilic*. If, however, the solid material refuses to return to the state of a sol, it is said to be *lyophobic*.*

In some modern books on colloidal solutions it will be found that the suspended particles are referred to as the "disperse phase" of the system. It should be noted that this employment of the word "phase," though convenient, is incorrect. A "phase" implies homogeneous physical character; and the particles in a colloidal solution are not necessarily physically homogeneous. In this connection it would be better to adapt to this use the word "phasis" employed by Graham and thus avoid the employment of a term which has a definite meaning in connection with the Phase Rule.

Most sols are capable of passing almost unchanged through filter-paper; so that ordinary methods of filtration fail to separate the suspended particles from the liquid in which they float. In the case of sols containing comparatively large particles, however, it is possible to remove some of the solid by means of *ultrafiltration*. Thus Linder and Picton[1] were able to separate some solid material from an arsenious sulphide sol by using a porous plate as a filter; and more recently[2] a graduated series of filters has been prepared by impregnating with a colloid gel some supporting sheet such as filter-paper, wire-gauze or fabric.

2. *The Preparation of Colloidal Solutions.*

The methods employed to produce colloid sols differ from each other according to the nature of the solid material which it is required to suspend in the liquid used; and it is therefore impossible within the scope of a few pages to deal in detail with the many processes which have been devised. All that need be attempted here is to outline the more characteristic ways of producing colloids and to restrict consideration to those methods which have a more or less general applicability.

(*a*) *Mechanical Dispersion.*[3]—In the case of such materials

[1] Linder and Picton, *Trans.*, 1892, **61**, 148.

[2] Bechold, *Zeitsch. physikal. Chem.*, 1907, **60**, 257; 1908, **64**, 328.

[3] Perrin, *Atoms*, 1916, p. 94.

* The terms "reversible colloid" and "irreversible colloid" are also used.

Digitized by Google

as gamboge it is possible to produce a colloidal solution by merely rubbing the grains with water. A simpler and better method, however, is to dissolve the gamboge as far as possible in alcohol and then pour the solution into water, which precipitates the gamboge colouring matter in the form of tiny spheres. Mastic can also be brought into the colloidal state by the same process.

(*b*) *Electrical Methods.*—Bredig[1] found that many metals may be reduced to the colloidal condition by using wires of them as electrodes in a small arc which is allowed to play under the surface of the liquid in which the metallic particles are to be suspended. In this way the metal is thrown off in tiny fragments which are sufficiently small to form a sol with the liquid. Owing to the possible fusion of soft metals when used in this manner, Svedberg[2] substituted for the direct current the oscillating discharge of an induction coil; and this method appears to be capable of more extensive use than the one devised by Bredig.

(*c*) *Chemical Methods.*—Under this head, three types of reaction may be considered: reduction, hydrolysis and double decomposition. Of these the reduction method is probably the oldest, for it was used in the preparation of Purple of Cassius (gold sol) as long ago as 1685. In modern days it was employed by Faraday[3] in his investigations upon colloidal gold. In the case of the Purple of Cassius, a solution of gold chloride is reduced by means of stannous chloride under certain conditions; and it is found that the metallic gold is thrown down in particles of colloidal magnitude. A somewhat similar process is to be found in the precipitation of sulphur when sulphuric acid is added to a solution of sodium thiosulphate. In this case, along with massive particles of sulphur some of the element is thrown out of combination in colloidal form.

The hydrolysis of the salts of weak acids and bases has been employed for the production of sols with some success, though of course it is not universally applicable. For example, if a solution of aluminium acetate be boiled for a time,

[1] Bredig, *Anorganische Fermente*, 1901, p. 22.

[2] Svedberg, *Kolloid Zeitsch.*, 1907, 1, 229, 257.

[3] Faraday, *Phil. Mag.*, 1857, 14, 401, 512; see also Zsigmondy, *Colloids and the Ultramicroscope*, 1909, pp. 124 ff.

Digitized by Google

it breaks down into aluminium hydroxide and acetic acid: and since the latter substance is volatile, it is removed from the solution as it is formed, leaving a colloid sol of aluminium hydroxide behind:—

$$Al_2(C_2H_3O_2)_6 + 6H_2O = Al_2(OH)_6 + 6CH_3COOH$$

Since the hydrolysis of the acetate is usually incomplete, it is necessary to subject the liquid to dialysis in order to purify it.

Double decomposition may take so many forms that only two examples need be given here; and it will be convenient to choose the preparation of an aluminium hydroxide sol again in order to illustrate the various ways in which a single colloid can be prepared. Taking the simplest case first, the action of water upon aluminium trimethyl gives rise to aluminium hydroxide. Since the second product of the reaction is the gas methane, only the hydroxide is left in the solution and a pure sol is obtained at once by this method:—

$$2Al(CH_3)_3 + 6H_2O = Al_2(OH)_6 + 6CH_4$$

By treating aluminium sulphate with ammonium hydrate, a sol of aluminium hydroxide is produced; but in this case it is contaminated with ammonium sulphate, which must be removed by dialysis:—

$$Al_2(SO_4)_3 + 6NH_4OH = Al_2(OH)_6 + 3(NH_4)_2SO_4$$

(*d*) *Conversion of Gel into Sol.*—The simplest case of this is the change of gelatine and water from the jelly-like condition into a liquid by raising the temperature of the mass. In some cases, the presence of electrolytes has a similar effect upon a gel. Thus Graham[1] showed that at 100° C. a trace of sodium hydroxide would convert a silicic acid gel into a sol. Another example of the same phenomenon is often observed during ordinary analysis in the case of aluminium hydroxide precipitates. In presence of a trace of an ammonium salt, the hydroxide is converted into the sol and when thus liquefied it passes through the pores of the filter-paper and escapes.

(*e*) *Action of a Colloid.*—When certain emulsoids such as solutions of starch, gum-arabic or gelatine are added to very dilute solutions of silver nitrate and potassium iodide, it is

[1] Graham, *Phil. Trans.*, 1861, **151**, 183.

Digitized by Google

found that the silver iodide produced on mixing the reagents is so finely-divided that it assumes the form of a sol. This "protective action" of the emulsoid seems to be due to the formation of a skin of colloid round the first tiny particles of precipitate, which are thus, in some way, prevented from coalescing to form larger aggregates.

3. *The Osmotic Pressure and Optical Properties of Colloidal Solutions.*

It has already been pointed out that a very striking difference between colloids and crystalloids is to be found in their relative capacity for diffusion. The figures below show the relative intervals of time which elapse before the same amount of substance is dialysed at a temperature of 10° C.

Colloids.		Crystalloids	
White of egg	49	Hydrochloric acid	1
Caramel	98	Sodium chloride	2·33
		Magnesium sulphate	7
		Sugar	7

From this extreme slowness of diffusion it is clear either that the force driving the colloid molecule (its osmotic pressure) is extremely small, or that the friction of its passage through the solution is very great. It is probable that both these factors play a part in the matter. Osmotic pressure measurements in colloid solutions show that the pressure is very small indeed, and the molecular weights of the colloids are probably of the order of 10,000. Sabanejeff and Alexandroff[1] found that white of egg has a molecular weight of about 14,000; and this is probably near the lower limit. These measurements depend upon the assumption that we are dealing with a true solution.

When a colloidal solution is examined with the naked eye, the liquid usually appears clear and transparent; but when a beam of light is concentrated and passed through the solution by means of a lens, it often gives rise to an appearance akin to fluorescence. Now if the fluorescent light emitted by a solution of quinine sulphate be examined, it is found that it is not polarised. On the other hand, the fluorescence of arsenic sulphide hydrosol yields polarised light. This fact brings the hydrosol question into a new aspect. It is well known that if a beam of

[1] Sabanejeff and Alexandroff, *J. Russ. Phys. Chem. Soc.*, 1891, **2**, 7.

Digitized by Google

light be thrown into a space filled with a gas in which fine particles are suspended, the light is polarised by reflection from the surface of the particles. The fact that light is polarised in colloidal solutions points to the necessity of determining whether or not they also are mere suspensions of particles. Naked eye observations are useless in this case. Microscopic investigations did not throw any very definite light upon the matter, though by means of them it was possible to assign a maximum diameter to the hypothetical particles. At last, by the invention of the ultramicroscope, it became possible to establish beyond doubt the existence of actual material bodies floating in the colloidal solutions.

The principle upon which the ultramicroscope depends can be illustrated by a very common phenomenon. In daylight, the air of an ordinary room appears perfectly clear to the naked eye, although it may be full of suspended dust-particles; but if the room be darkened and a simple beam of light be then admitted the floating dust of the air becomes visible in the path of the beam as a series of motes dancing in the ray.

Faraday[1] appears to have been the first* to apply this principle to the examination of colloidal materials; but the originator of the ultramicroscope in its modern form was Zsigmondy.[2] In the original form of the instrument the field of a microscope is illuminated at right angles to the optical axis of the instrument; and the particles floating in the liquid appear as bright specks upon the dark field: but more recently different methods of illuminating the field have been devised. In every case, the main point of the method lies in the fact that although a particle itself may be too small to be detected by the microscope, the flash of light which it reflects is sufficient to allow its presence to be recognised; and thus the number of particles in a small volume of the colloidal solution may be estimated with a fair degree of accuracy. By means of the ultramicroscope it is possible to detect the presence of particles having a diameter not less than 0·000005 mm.

[1] **Faraday**, *Proc. Roy. Inst.*, 1854-8, **2**, 310, 444.

[2] Zsigmondy, *Erkenntniss der Kolloide*, 1905; *Colloids and the Ultramicroscope*, 1909.

* The phenomenon is, however, generally known as the "Tyndall Effect" (Tyndall, *Phil. Mag.*, 1869, **37**, 384; *Proc. Roy. Soc.*, 1869, **17**, 223).

Digitized by Google

When the ultramicroscope is applied to the study of colloidal solutions it reveals the fact that colloids are not necessarily uniform in character. Organic colloidal materials such as albumen are found to contain masses of varying size, some of these floating groups being comparatively large whilst others are so small as to evade exact ultramicroscopic examination. On the other hand, colloidal solutions of the metals are found to contain small independent particles; and in the case of some metals it has been possible to arrive at rough estimates of the sizes of these metallic specks. The following figures give some idea of the approximate diameters of some of these objects:—

Particles in	Approximate diameter.
Gold hydrosol	0·02 to 0·08 mm.
Platinum hydrosol	0·044 mm.
Silver hydrosol	0·05 to 0·077 mm.

In some gold hydrosols the metallic particles have diameters no greater than 1·7 microns; and since the diameter of the hydrogen atom as deduced from the kinetic theory of gases is 0·00016 micron, it follows that these gold particles are only ten thousand times the size of a hydrogen atom in linear dimensions.

In connection with light, another property of colloidal metallic solutions may be mentioned here. Gold hydrosols vary in colour with transmitted light from rose-tint to blue, according to the nature of the solution; and by centrifuging a colloidal gold solution Lampa[1] was able to produce a tube in which the tint varied uniformly from red at the top to blue at the bottom. Since the more massive particles tend, under centrifugal action, to accumulate in the lower layers of the solution, this goes to prove that in the red solutions the gold particles are finer than in solutions showing a blue colour. According to Zsigmondy,[2] the rose-tinted gold hydrosols contain particles with an average diameter of $6\mu\mu$ whilst the blue hydrosols are suspensions of particles reaching $130\mu\mu$ in diameter. From an examination of the colours of various colloidal solutions, Wo. Ostwald[3] draws the conclusion that as the size

[1] Lampa, *Sitzungsber. Akad. Wiss. Wien*, 1909, **118**, II.*a*, 1565.
[2] Zsigmondy, *Erkenntniss d. Kolloide*, 1905, p. 104.
[3] Wo. Ostwald, *Koll. Chem. Beih.*, 1901, **2**, 409.

Digitized by Google

of the particles in the colloid is diminished the absorption band of the colloidal solution moves toward the shorter wavelengths of the spectrum.

4. *The Electrical Properties of Colloidal Solutions.*

In the electrochemistry of colloidal solutions, two lines of inquiry are open: for in the first place it may be asked whether all such solutions (some of which apparently contain no ions of the ordinary type) exhibit a conductivity different from that of the pure solvent; and in the second place investigation may be instituted to discover relations between the nature of the colloid and the pole to which it moves, always supposing that such movement actually takes place.

With regard to the first of these problems, the experimental results obtained up to the present hardly permit any general conclusion to be drawn. It must be borne in mind that the solid particles in colloidal solutions differ so much in chemical character that generalisation is almost impossible. For instance, consider three typical colloids: a platinum sol; a solution of albumen; and a sol containing suspended ferric hydrate. Particles of metallic platinum cannot be assumed to yield ions in the usual sense of the word; albumens are built up from amino-acids which contain both oxygenic and basigenic radicles and their electrical character is almost indistinguishable from neutrality; whilst ferric hydroxide is a basic material. Thus to expect marked similarity in behaviour from all three is to make the assumption that the colloidal state exerts a preponderating influence upon electrical character; and this postulate is by no means easy to grant. Further, before the electrochemical character of the colloids themselves can be ascertained it is essential to show that every trace of ordinary electrolytes has been removed from the solution, which is not readily established in practice.

In order to illustrate the difficulty of proving the absence of normal electrolytes from solution, an example may be taken from the work of Whitney and Blake.[1] The most certain method at our disposal for the removal of ions from solution is to subject the electrolyte to a series of successive electrolyses.

[1] Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, **26**, 1339.

Digitized by Google

In the case of a gold sol, Whitney and Blake obtained the following results. The solution was subjected to dialysis in the first place.

	Specific conductivity × 10^6.
After dialysis	13·2
„ 1 electrolysis	7·7
„ 2 electrolyses	4·2
„ 3 „	2·7
„ 4 „	2·1
„ 5 „	1·8
For the water used in sol-formation	1·3

From these results, Whitney and Blake conclude that the values are converging to a definite figure which is regarded by them as being the true conductivity of the gold sol; but as Taylor[1] points out, it is quite as reasonable to suppose that the figures are converging upon the value 1·3, since by extrapolation of the graph this number would be reached after three further electrolyses.

In spite of the number of investigations carried out in this field, the question cannot be regarded as settled, so far as these metallic sols are concerned.

When the second of the two problems propounded above is examined, the results are much more definite. Certain colloidal solutions can be sharply divided into two classes according as their particles move towards the cathode or the anode; and it is evident that in the former case the solid part of the sol carries a positive charge whilst in the second group the charge on the particles is negative.[2] The following list[3] of hydrosols gives some idea of the members of the two classes:—

Particles negatively charged.	Particles positively charged.
Sulphides of As, Sb and Cd	Hydroxides of Fe, Cr, Al, Cu and Th
Sols of Pt, Ag, Au and Hg	Sols of Bi, Pb, Fe and Cu
Stannic acid and silicic acid	Titanic acid
Indigo, eosin, fuchsin	Magdala red, Bismarck brown, methylene blue
Starch, mastic, lecithin	Albumen, hæmoglobin, agar

This migration of colloid particles toward one or other of the electrodes is termed *cataphoresis*. In some cases the phenomenon appears to be influenced by the nature of the solution.

[1] Taylor, *Chemistry of Colloids*, 1915, p. 63.
[2] Picton and Linder, *Trans.*, 1892, **61**, 148.
[3] Burton, *Physical Properties of Colloidal Solutions*, 1916, p. 126.

Digitized by Google

Thus globulin and silicic acid are said to travel toward the anode in alkaline solutions but toward the cathode when the solution is acidic.[1]

It can be calculated[2] that the velocity of a series of particles suspended in a liquid between two electrodes is given by the equation—

$$v = \frac{\epsilon DH}{4\pi\eta}$$

wherein v = velocity of particles; ϵ = dielectric constant of the liquid; D = the potential difference between the particles and the liquid; H = fall of potential difference between the electrodes in volt/cms.; and η = viscosity of the liquid. Inspection shows that this equation contains no term representing the magnitude of the particles; whence it appears that this can have no influence upon their velocity. By assuming that the particles were composed of glass, and then by substituting the known values of the various constants in the equation, Smoluchowski[3] calculated that this velocity should be 34×10^{-5} cms. per second. Actual measurements[4] in the case of metallic sols and sols of arsenic sulphide and of ferric hydroxide indicate that the particles in these liquids have velocities lying between 19×10^{-5} and 33×10^{-5}; which is sufficient to prove that the potential differences between water and all these various solid particles are of the same order as that between glass and water. Further, since the solid particles in the various sols were very different in diameter, it is clear that the velocity is independent of the size of the particles, as the theory predicts. It is not without interest to note that this velocity is almost identical with that of certain slow-moving ions under the same conditions. For example, the sodium ion moves at the rate of 45×10^{-5} cms. per second; whilst the lithium ion has a velocity of 36×10^{-5} cms. per second for a fall in potential of one volt per cm. From these values it appears that the velocity of the suspended particles

[1] Burton, *Physical Properties of Colloids*, 1916, p. 127.

[2] See Taylor, *Chemistry of Colloids*, 1915, pp. 66, 76; Burton, *Physical Properties of Colloidal Solutions*, 1916, p. 127.

[3] Smoluchowski, *Bull. Acad. Scien. Cracow*, 1903, 182.

[4] Linder and Picton, *Trans.*, 1897, 71, 508; Whitney and Blake, *J. Amer. Chem. Soc.*, 1904, 26, 1339; Burton, *Phil. Mag.*, 1904 (vi), 11, 425; Cotton and Mouton, *Ann. chim. phys.*, 1906, 4, 363.

Digitized by Google

in a colloid under electrical stress is for all practical purposes identical with that of some ions.

In the cases considered above, the chemical character of the suspended particles is well marked; but when more complex materials are examined the results indicate that a further factor must be taken into consideration. Compounds such as gelatine and egg-albumin, being built up from amino-acid chains, have no marked positive or negative electrical character but contain both oxygenic and basigenic radicles. This fact might enable us to predict the course of the cataphoric phenomena actually observed [1] in aqueous solutions of these materials. In neutral solution, albumin shows no cataphoresis at all; in an acid solution the particles migrate toward the cathode; whilst in alkaline solutions the process is reversed and the particles move toward the anode. It is not, of course, certain that the amphoteric character of the compound is the root-cause of this behaviour; for it may just as easily be assumed that the colloid is iso-electric with regard to water and picks up either a positive or a negative charge according to the ions with which it becomes associated in solution. The fact that a suspension of petroleum in water acquires a negative charge although it has no positive or negative radicles in its structure seems to indicate that the amphoteric nature of the albumins has some influence upon their behaviour.

Against this, however, there is a certain amount of evidence drawn from another field. When a porous diaphragm or a capillary tube is placed between two electrodes in a liquid, it is found that there is a movement of the liquid through the membrane or tube when the current passes through the liquid. This naturally leads to the establishment of a difference between the levels of the liquid on either side of the diaphragm; and the phenomenon is termed *electro-endosmosis* from its resemblance to the effects observed in osmotic cells.

Wiedemann [2] discovered that, when other conditions are constant, the difference in level depends on the viscosity of the solution and the E.M.F. applied. Since viscosity enters

[1] Perrin, *Compt. rend.*, 1903, **136**, 1388; Hardy, *J. Physiol.*, 1904, **24**, 288; Pauli, *Beitr. chem. Physiol. Path.*, 1906, **7**, 531.

[2] Wiedemann, *Ann. d. Physik*, 1852 (ii), **87**, 321.

Digitized by Google

into the problem, it is clear that at some stage in the phenomena friction between two layers of material must play its part; and it is assumed that both these layers are liquid, the one being in motion whilst the other adheres fixedly to the solid material of the diaphragm. The further assumption is made that the two liquid layers carry charges of different potentials.

On this basis, the following equation has been worked out, which appears to concord with the experimental results:—

$$V = \frac{eqDE}{4\pi\eta l}$$

in which V = volume of liquid transferred across the diaphragm; e = dielectric constant of the liquid; q = area of diaphragm; D = potential difference between the two liquid layers; E = E.M.F. at the electrodes; η = viscosity of the liquid; and l = distance between the electrodes.

A simpler equation is obtained when pressure is measured instead of volume, by allowing the liquid to rise in a tube and measuring the height which it attains. The following equation should then hold good:—

$$P = \frac{2eED}{\pi r^2}$$

in which r is the radius of the tube and the other symbols have the same meanings as before. If this equation be correct and if the measurements be made in tubes of the same material, then obviously the height to which the liquid will rise in any experiment is proportional directly to the applied E.M.F. and inversely to the square of the radius of the tube. From experiments with glass capillaries and varying E.M.F.'s, Quincke[1] established the truth of the equation, showing that the factor D is constant, being equal to the potential difference between glass and water.

With the exception of some basic oxides and hydroxides and a few salts, all substances when placed in contact with water become negatively charged; and in this case the water travels toward the cathode in electro-endosmosis. But it is found that the difference in potential between the two layers may be altered by the addition of solutes to the water; and

[1] Quincke, *Ann. d. Physik*, 1861 (ii), **113**, 513.

Digitized by Google

this contamination may increase or diminish the potential difference, so that there may even be a change of sign due to the process.

The researches of Perrin[1] have thrown light upon this region of the subject. He constructed a series of porous diaphragms from glass tubes of about 10 cms. in length and 1·5 sq. cm. in cross-section, the tubes being packed with the insoluble material which formed the actual diaphragm, In this way Perrin was able to examine the behaviour of aluminium oxide, naphthalene, chromium chloride, silver chloride, barium sulphate, boric acid, sulphur, salol, carborundum, gelatine, cellulose, zinc sulphide, calcium carbonate, barium carbonate, manganese trioxide and powdered glass. The liquids employed were solutions of acids, bases and salts; and it was found that the solutions were drawn by the current toward one or other of the electrodes, between which there was a fall in potential of about 10 volts per cm. across the diaphragm. The direction of liquid flow depended upon the nature of the solution but was independent of the composition of the insoluble diaphragm. Only liquids of high dielectric constant—*i.e.*, those with high dissociating power—exhibited appreciable electro-endosmosis. His results showed that the addition of a monovalent acid to an aqueous solution always raises the electric potential of the wall of the diaphragm, whilst the addition of a monovalent base to the solution has the opposite effect and lowers the wall's potential. If contact with a certain liquid produces on the diaphragm wall a charge of a certain sign, this electrification can be reduced and even changed in sign by adding to the liquid a polyvalent ion of the opposite sign. Monovalent ions have the feeblest influence; and the effect increases with the increase in the valency of the ion, as the following figures show. The diaphragm in this case was a negatively-charged one of carborundum in alkaline solution:—

Salt added.	Volume in c.c. per minute.
0	− 60
0·1 m. NaBr	− 14
0·002 m. $Ba(NO_3)_2$	− 26
0·0002 m. $La(NO_3)_3$	− 18

[1] Perrin, *J. chim. phys.*, 1904, **2**, 601; 1905, **3**, 50; see also Elissafof, *Zeitsch. physikal. Chem.*, 1912, **79**, 385.

Digitized by Google

It will be noted in the above figures that the concentration of the trivalent ion of lanthanum is ten times less than that of the divalent barium ion, whilst the effect produced by it is greater than that of the barium one. It must be borne in mind that in this case we are concerned with a negative diaphragm and that the positive ion is the controlling factor in the change. This can be proved by considering the case of another negative diaphragm in presence of salts with a common magnesium ion. For the chromic chloride diaphragm in alkaline solution the following results were obtained:—

Salt added.	Volume in c.c. per minute.
0·0	− 76
0·001 m. $MgCl_2$	− 10
0·001 m. $MgSO_4$	− 6

Here, it is clear, the difference between the monovalent chlorine ion and the divalent sulphate ion produces very little change in the volume of water forced through the membrane.

In the case of a positive diaphragm, such as chromic chloride in contact with an acid solution, the results show that the addition of 0·0005 m. of potassium ferricyanide has a much greater influence than 0·1 m. of potassium bromide; so that in the case of the positive diaphragm the valency of the acidic ion is the main factor.

These results may be summarised as follows: The electrical charge on a diaphragm is reduced by the presence in solution of an ion of the opposite sign and the magnitude of the effect increases with the valency of that ion and is independent of the valency of the second ion of the salt employed. In the absence of polyvalent radicles, all non-metallic substances become positively charged in acidic liquids and negatively charged in basic liquids.

Returning now to the cataphoresis of albumins, it is evident that the charges upon these materials in solution may be due to simple charging of their particles and need not necessarily be ascribed to their amphoteric character. In Perrin's investigations, as has been mentioned above, a diaphragm of naphthalene acquires a charge which cannot be ascribed to the electrochemical nature of the compound's constitution; and it is therefore not unwarranted to assume

Digitized by Google

that albuminous materials may become charged in a similar manner and thus become capable of cataphoresis independently of any ionisation which they undergo.

5. *The Catalytic Action of Sols.*

Some metallic sols have a well-marked catalytic action in the case of certain reactions.[1] For example, when 2·5 cubic cms. of a platinum sol containing 0·17 mgr. of platinum were shaken with electrolytic gas, it was found that the gaseous volume rapidly diminished owing to a combination of the oxygen and hydrogen to form water. The following figures were obtained by Bredig:—

Time in minutes	10	20	30	40	50
Decrease in volume of gas	17·8	35·8	54·8	72·4	90·2 c.c.

Similar results are observed in the case of the decomposition of hydrogen peroxide, which is hastened by the presence of colloidal metals.

The catalytic action in these cases is probably to be ascribed to the great metallic surface which is exposed when metals are reduced to the colloidal state, since even ordinarily finely divided metals exert a powerful catalytic influence upon certain reactions.

A peculiar phenomenon is observed when certain substances are added to these metallic sols: apparently they lose their power of accelerating reactions, just as some organic enzymes cease to act as catalysts in presence of "poisonous" compounds. For instance, the decomposition of hydrogen peroxide by platinum sol ceases to be catalysed when the solution contains in addition one part of hydrocyanic acid in 20×10^6 or one part of mercuric chloride in 25×10^5.

Since these compounds also "poison" the organic enzymes, Bredig was led to draw a somewhat fanciful parallel between colloidal metals and organic ferments; but it seems probable that the common factor is merely surface action.

6. *Coagulation.*

Hitherto this chapter has dealt mainly with the properties of colloids in the sol form; but at this point it seems advisable

[1] Bredig and Berneck, *Zeitsch. physikal. Chem.*, 1899, 31, 258; Ikeda, *ibid.*, 1901, 37, 1; Reinders, *ibid.*, 323; Ernst, *ibid.*, 448.

Digitized by Google

to discuss the conversion of the sol into the gel and *vice versâ*. When a gel is produced from a sol, the process is termed *coagulation*.*

Classification of the methods whereby coagulation can be produced is difficult, owing to the variety in the conditions which may produce the agglomeration of the suspended particles. For example, certain sols are converted into gels by simple heating; but this is by no means a general rule, for in some cases gels are changed to sols by raising the temperature. Again, coagulation is in some cases brought about by adding electrolytes to the sol form; but there are exceptions here also. The addition of non-electrolytes fails to produce coagulation in most inorganic colloids, though an organic colloid like egg-albumin is precipitated from aqueous solution by alcohol. Even from these examples it becomes clear that a classification of the coagulation processes according to the nature of the coagulating agent presents marked difficulties.

There is, however, another set of phenomena which enables a rough division to be made between two parts of the subject. It is found that in some colloids the conversion of sol into gel is a reversible process whilst in other cases the gel is not reconvertible into the sol directly. It is therefore possible to separate the field of coagulation into two parts, in one of which are placed examples of *reversible coagulation* whilst the other contains cases of *irreversible coagulation*. But even this classification breaks down in some instances, for colloids are known which might be regarded as falling into either class according to the conditions of experiment. It will be best to give concrete examples to illustrate the differences between the various phenomena.

The case of irreversible coagulation being the simplest, it will be well to deal with it first. When solutions of arsenious acid and sulphuretted hydrogen are mixed together, arsenious sulphide is produced; but as it exists in the sol form, no precipitate is formed. The addition of acids or salts, however, produces an immediate precipitation of the arsenious sulphide in the form of a gel. The process in this case is irreversible; for the sediment cannot again be brought into solution.

* The terms "solation" and "gelation" have been proposed in order to distinguish the two processes of sol-production and gel-formation.

Digitized by Google

Another example of irreversible coagulation is furnished by boiling an egg, whereby the rise in temperature converts the sol into a gel. The process is obviously irreversible, since there is no known method of "unboiling" white of egg once it has been coagulated.

For an example of reversible coagulation, it is unnecessary to go further than glue or gelatine. Warm solutions of these substances exist as sols which on cooling, if the concentration be sufficient, will congeal into very obvious gels; and on again raising the temperature, the gel will liquefy and become re-converted into the sol form.

Finally, to illustrate the third type, in which the coagulation process may be either reversible or irreversible according to the conditions chosen, the example of silicic acid will suffice. When a silicic acid sol is allowed to evaporate slowly at ordinary temperatures it yields a glassy material from which the sol can again be obtained by simple addition of water. This is clearly a case of reversible coagulation. But if the water be completely removed from the glassy material by heating it, some change in the nature of the solid takes place and it is then incapable of forming a sol on the addition of water.

In connection with coagulation, one of the most interesting points is to be found in the relations between a colloid and an electrolyte. If to a colloid sol under the ultramicroscope there be added a solution of a salt, it is found that certain changes can be traced in the dark field of the instrument. The pure sol is represented by points of light in very rapid movement. With the addition of the electrolyte, the minute particles of the sol coalesce and form aggregates which appear as tiny illuminated discs, still in extremely rapid motion. The presence of greater quantities of electrolyte conduces to a further aggregation of the particles and to a slowing of their motion; and the groups of particles increase in magnitude and diminish in velocity until movement entirely ceases and sedimentation of the precipitate begins.

Three possible explanations of these phenomena suggest themselves. In the first place, the process might be assumed to be parallel ionic precipitation or to the salting out of one reagent by another. Secondly, the influence of the electrolyte

Digitized by Google

might be due to its acting as a "brake" on the motion of the particles and thus, by slowing down their vibrations, permitting them to cling together and become sedimented. Or, finally, the particles may tend to coalesce more eagerly in presence of the electrolyte and the slowing of their motion may be a mere result of the increase in size of the aggregates.

The improbability of the first explanation is easily made clear.[1] In the case of ordinary analytical precipitations, the precipitant is decomposed during the process; whereas in the case of colloids the precipitating reagent remains chemically unchanged, as far as we know. Nor can the parallelism with the salting-out process be maintained, for in salting out it is necessary to add a very large quantity of the precipitant, whereas in the case of colloids a comparatively small amount of electrolyte will bring about coagulation.

The second explanation can be disposed of even more conclusively. Svedberg, by direct observation, found that in the case of a silver sol to which aluminium sulphate was added there was no change in the amplitude of the vibration of the particles on the addition of the electrolyte; but that as the particles coalesced the amplitude of vibration diminished with each increase in size of the aggregates. This proves that the change in the velocity of the particles is the result and not the cause of the coagulation; so that the field is left free for the third explanation mentioned above.

Before dealing with the theory of this, however, it is necessary to examine the phenomena in more detail, for several points must be made clear if the problem is to be understood.

The work of Schulze[2] and of Linder and Picton[3] established the fact that when an electrolyte is gradually added to a colloid sol, no coagulation takes place until the concentration of the salt reaches a certain minimum value. When less than this minimum quantity of electrolyte is present, the sol remains stable. For example, when the amount of sodium chloride necessary for the complete precipitation of a ferric hydroxide sol has been ascertained, it is found that the sol will tolerate

[1] Hardy, *J. Physiol.*, 1905, **33**, 258.
[2] Schulze, *J. pr. Chem.* (2), 1882, **25**, 431; 1883, **27**, 320; 1884, **32**, 390.
[3] Linder and Picton, *Trans.* 1905, **87**, 1992.

Digitized by Google

the presence of one-sixth of this quantity of sodium chloride without apparent coagulation; for it remains clear even when boiled with this proportion of the salt. Again,[1] when three equal portions of an arsenious sulphide sol were treated with potassium chloride so that one portion contained 1·219 millimols of chloride per litre whilst the second held 2·438 millimols per litre, and the third contained 3·90 millimols of salt, it was found that the first two solutions were hardly affected at all, whereas the third one gave complete precipitation of the arsenious sulphide.

From these results it is clear that the mere presence of the electrolyte is not sufficient to produce coagulation; but that the concentration of the electrolyte must attain a certain minimum value—sometimes called the precipitation concentration—in order that the colloid may be thrown down.

This is not, however, the only peculiarity of the process; for a much stranger phenomenon remains to be described. In an ordinary chemical reaction we are not concerned with the previous history of the reagents which play a part in it. One gramme molecule of hydrochloric acid will always suffice to precipitate completely from silver nitrate solution one gramme molecule of silver chloride; and the amount of hydrochloric acid required is the same no matter whether it is added in one operation or step by step. In the case of the action of electrolytes upon colloids, however, the process does not follow this rule; for the manner in which the precipitant is added has a marked influence upon the course of the reaction. For example, if the amount of barium chloride sufficient to precipitate an arsenious sulphide sol in one operation be determined, it is found that when the same quantity of barium chloride is added to the sol in small quantities at a time, precipitation is by no means complete and a much larger amount of the salt must be added to ensure complete coagulation. In fact, by treatment with barium chloride in small doses, the sol appears to become less sensitive to the action of the salt, just as a human being can be trained into a partial immunity to arsenic by giving him minute doses from time to time, or as a mild attack of a disease may render a living organism more resistant to a

[1] Freundlich, *Zeitsch. physikal. Chem.*, 1903, **44**, 144.

Digitized by Google

second attack. It seems, therefore, that in this colloid field phenomena make their appearance which faintly though distinctly recall certain processes which take place in living organisms. The agglutination of bacteria which forms the basis of Widal's reaction in the diagnosis of typhoid fever furnishes an example of an analogous phenomenon.

When the precipitating action of electrolytes upon colloids is examined, two important facts are discovered. In the first place, the precipitating power of the electrolyte resides in the ion whose electrical charge is opposite to that on the sol, so that a basic sol is coagulated by an anion whilst an acidic sol is sensitive to the influence of cations. Secondly, the effect produced by a given ion is related to the valency of the ion. A monovalent ion has less influence than a divalent one, and the divalent ion in turn has less action than a trivalent ion. For example, in the case of a sol of arsenious sulphide, the coagulating ion is a positive one; and if the relative concentrations of electrolyte required to produce precipitation of the colloid be determined in the cases of potassium nitrate, barium nitrate and aluminium nitrate, it is found[1] that they stand in the following order:—

Potassium nitrate	50·0
Barium nitrate	0·687
Aluminium nitrate	0·095

Thus a minute concentration of the trivalent aluminium ions will produce the same effect as a seven-fold concentration of divalent barium ions; and the effect of the monovalent potassium ion is so small that the concentration of them must reach five hundred times that of the aluminium ions in order to do the same work. Both in electro-endosmosis and in coagulation the charge on the ion appears to play a very large part in the phenomena.

From the facts given above with regard to cataphoresis, it is evident that this phenomenon can be accounted for by assuming that certain colloids carry a positive charge, whilst others are negatively electrified. This assumption agrees, further, with the results which have just been described in the case of the coagulation of sols by means of ions; since the

[1] Freundlich, *Zeitsch. physikal. Chem.*, 1908, **44**, 144.

Digitized by Google

collision of a positively charged ion with a negatively charged colloid would rob the colloid of its charge and reduce it to the state of an ordinary suspension. It now remains to put the matter to a final test by determining what effect, if any, is produced when two colloids of opposite charge are brought into contact.

Linder and Picton[1] were the first to observe that when two oppositely charged colloids were mixed, both became precipitated. Later on, Lottermoser[2] found that ferric hydroxide, for example, would cause the coagulation of silicic acid when the two were mixed in sol form. To a certain extent there is a resemblance between the action of a sol and an ion of similar charge. For example, just as the ions act differently according as they are added bit by bit or *en masse* to the sol which they precipitate, so the precipitating action of one sol upon another varies according to the manner in which they are mixed. Further, just as a certain concentration of ions is required to produce coagulation, so the precipitating colloid must reach a minimum concentration before it acts measurably upon the second sol. At this point, however, there is a divergence between the two phenomena; for when one colloid A is added by stages to a second colloid B it is found that the following phenomena take place, provided that the two colloids are rapidly and thoroughly mixed together: (1) a small quantity of A fails to precipitate B; (2) a larger quantity of A precipitates B; (3) a still larger quantity of A fails to produce the coagulation of B which was easily obtained by using a smaller quantity of A. In other words, there is a certain "optimum concentration" of A which produces the maximum precipitation of B; and any quantity of A either larger or smaller than this will fail to produce such satisfactory results.[3]

There is a further resemblance between the actions of colloids and ions which must be mentioned here. It is found that in the case of a positively charged sol, the presence of hydrogen ions in the solution makes the colloid much less susceptible to coagulation; whilst the coagulation of a negative sol is analogously inhibited by the presence of hydroxyl ions.

[1] Linder and Picton, *Trans.*, 1897, 71, 568.
[2] Lottermoser, *Anorganische Kolloide*, 1901, p. 77.
[3] Biltz, *Ber.*, 1904, 37, 1095.

Digitized by Google

The ions appear to "protect" the colloid from the attacks of oppositely charged ions, just as might be expected. Now, as was first shown by Linder and Picton,[1] there is a very intimate relationship between colloids and ions; for when the negative arsenious sulphide sol is precipitated by adding barium chloride to the solution, it carries down with it a very large proportion of barium, and the remaining liquid acquires acid properties owing to the excess of chlorine ions left in it. The barium is so firmly retained by the precipitate that no washing with water will suffice to remove it; and it is said to be *adsorbed* by the colloid.

This process is suggestive when it is considered in connection with another "protective" action. Faraday[2] observed that in presence of "jelly" * a gold sol was more stable than it seemed to be in the pure state; so that the "jelly" had a protective influence upon the sol and hindered its coagulation. This phenomenon appears to be of a general character. When gelatine, albumin, gum-arabic or any other *stable* colloid is added to a less stable sol, such as silver sol, it is found that the less stable sol is protected by the presence of the more stable one and becomes much more difficult to precipitate.[3]

Zsigmondy[4] devised a method by means of which this phenomenon can be studied quantitatively. Using a gold sol obtained by reducing gold chloride in solution by means of formaldehyde, he measured the weight in milligrammes of a colloid which just fails to prevent the colour-change of red to violet in a mixture of 10 c.c. of his standard sol and 1 c.c. of a 10 per cent. sodium chloride solution. This weight Zsigmondy christened the "gold number" of the colloid in question; and obviously the smaller the gold number, the greater the protective power of the colloid. Some examples of gold numbers will show the great differences between the protective power of various colloids.

[1] Linder and Picton, *Trans.*, 1895, **67**, 63.

[2] Faraday, *Phil. Trans.*, 1857, **147**, 154.

[3] Meyer and Lottermoser, *J. pr. Chem.*, 1897, **56**, 241; Lottermoser, *Anorganische Kolloide*, 1901, p. 50.

[4] Zsigmondy, *Zeitsch. analyt. Chem.*, 1902, **40**, 697.

* His "jelly" was probably gelatine.

Digitized by Google

Colloid.	Gold Number.
Gelatine	0·005 to 0·01
Egg-albumin	0·15 to 0·25
Gum tragacanth	2 (approx.).
Potato starch	25 (approx.).

It is not only the organic colloids which can act as protectors; for silicic acid sols have similar properties and zirconium hydroxide sols exceed even gelatine in protective power. It must be remembered, however, that the efficiency of the protection afforded is dependent upon various factors and differs from sol to sol.

A possible explanation of the protective power is to be found in the phenomena of adsorption.* If the particles of the unstable colloid be coated with an adsorbed layer of the stable colloid, the properties of the unstable sol will then approximate to those of the stable coating; and hence there will be an increased resistance to coagulation in the mixture.

7. *The Properties of Gels.*

The coagulation of a colloidal solution may give rise to either of two products, according to the nature of the colloid. In the case of metallic sols, the solid particles are precipitated from solution in the form of a loose powder which is not necessarily associated with the liquid material of the sol. In other types of sol, however, a gel is produced by the coagulation process; and in this gel both the components of the liquid colloid are present. The gels themselves, as has already been mentioned, can be divided into two classes according to their behaviour on drying. The members of the lyophobic class, when dried, refuse to absorb the solvent again; whereas the lyophilic gels have the property of re-forming sols when wetted with the solvent. Gels can also be classified as "elastic gels" and "non-elastic gels," according to their behaviour on stretching.

With regard to the proportions of water found in gels, it has been established by van Bemmelen[1] that these are quite arbitrary in most cases. Gels of silica, stannic oxide, ferric oxide and aluminium oxide are found to contain proportions of

[1] van Bemmelen, *Ber.*, 1878, **11**, 2232; 1880, **13**, 1466.

* See Chapter XIII.

Digitized by Google

water which indicate that the quantity of liquid present in the gel is governed by external conditions and corresponds in no way to molecular ratios. In the case of silicic acid gels, the materials are unstable systems of the general formula

$$SiO_2, nH_2O,$$

the value of n being dependent on physical conditions and also, strange to say, upon the previous history of the substance. Owing to this last fact, it is evident that with the chemistry of colloids a step is being taken from the hard-and-fast lines of pure chemical action towards the field of biochemistry.*

Among the elastic gels, of which gelatine is a good example, the action of water is of considerable interest. When water is placed in contact with solid gelatine, the system undergoes a contraction in volume, though the gelatine itself swells in bulk and heat is evolved during the process. The pressure produced by this swelling of the gelatine is by no means negligible, for in some cases it is sufficient to burst a porous pot.[1] There is no evidence of chemical combination between the gelatine and water; but the elastic gels differ from the non-elastic ones in the fact that after an elastic gel has come into equilibrium with water vapour it can still take up further quantities of water if it is placed in contact with liquid water. When gelatine is placed in contact with salt solutions it is found that it takes up both water and the solute; and the nature of the solute influences the amount of water which the gelatine absorbs.[2] For example, if equal quantities of gelatine be placed in contact with sodium sulphate solution, pure water and sodium chloride solution, it is found that the greatest absorption occurs with the sodium chloride solution and the least absorption takes place in the sodium sulphate solution.

With regard to the physical properties of gels, it is found that the expansion of a gel on heating is practically the same as that of the water (or other liquid) which it contains. The compressibility of the gel is much greater than that of the solid material. Investigation shows that when a gel is stretched

[1] Schroeder, *Zeitsch. physikal. Chem.*, 1903, **45**, 109.

[2] Hofmeister, *Archiv. exp. Physiol. Path.*, 1891, **28**, 210, 238.

*Since colloids form the major part of the substances composing the chemical basis of living tissue, it is obvious that biochemical reactions must be largely influenced by the properties of matter in the colloidal state.

Digitized by Google

it suffers no change in volume. One very curious property of gels must be described, since it shows that these materials, though not solids, can nevertheless be "strained," just as glass is strained, by unequal heating or by external force. By placing a gel in an annular vessel of which the inner wall was rapidly rotated whilst the outer one was kept fixed, it was found that under these conditions the gel showed double refraction, just like unannealed glass. This effect is not due to the viscosity of the gel, for when solutions of glycerine of greater viscosity were examined, no such phenomena were detected.

An interesting property of gels is exhibited in the formation of what are known as Liesegang's rings. When a horizontal glass plate is coated with a gelatine sol to which some ammonium bichromate is added and, after the gelatine has set and before it becomes dry, a drop of silver nitrate is placed in the centre of the sheet, it is found that a series of concentric rings of silver bichromate are produced around the original position of the drop. Between the rings, there is no marked deposit of precipitate; and the rings are formed at ever-increasing distances apart as they spread out from the centre.

Ostwald[1] suggested an explanation for this phenomenon; but it seems mainly remarkable for the fact that it fails to account for the most obvious part of the results. In his view, an excess of silver ion is required to produce supersaturation in the metastable region, whereby nuclei of the precipitate may be formed. As soon as these nuclei are formed, according to him, the whole of the local silver bichromate is thrown down, with the result that the silver ions have to travel a considerable distance further before they meet enough bichromate to induce precipitation again. Against this conception of the process, several objections may be urged. In the first place, on Ostwald's assumptions, precipitation ought to be most marked at the centre of the drop, which is exactly where no precipitate is produced in practice. Secondly, the hypothesis leaves out entirely the possible protective action of the colloid on the precipitated silver bichromate (sol) although the protective action of gelatine is known to be very marked.

[1] Ostwald, *Lehrbuch*, 2, II., 778.

Digitized by Google

It seems much more probable[1] that Ostwald's "explanation" is the very reverse of the truth. When a very dilute solution of silver nitrate is added to dilute potassium iodide it is found that a silver iodide sol is produced which is stable so long as excess of potassium iodide is present. As soon, however, as the silver and iodine ions are present in exactly equal quantity, the sol is precipitated.[2] On this basis, the precipitation which gives rise to Liesegang's rings should occur only where the silver and bichromate ions are present in exactly equal quantities; whilst where one of them is in excess—as in the centre of the original drop, only silver bichromate sol would be formed and no precipitation would take place.

Another attempt[3] to account for the production of Liesegang's rings has been made, the basic assumption in which is the existence of gelatine in two forms, α-gelatine and β-gelatine. Ultramicroscopic observation seems to show that ordinary gelatine is built up from an irregular network of fibres, between which lies a structureless mass; and it appears that the diffusion of any electrolyte into gelatine gives rise to laminated structures, quite independently of chemical action. The production of the Liesegang rings and analogous phenomena is therefore ascribed to the influence of the structural basis of the gel, the orientation of the α-gelatine fibres being the governing factor in the problem.

[1] Taylor, *Chemistry of Colloids*, 1915, p. 147.
[2] Lottermoser, *J. pr. Chem.*, 1905, **72**, 39; 1906, **73**, 374.
[3] Moeller, *Kolloid Zeitsch.*, 1916, **19**, 205, 213; 1917, **20**, 242, 257.

Digitized by Google

CHAPTER X.

THE BROWNIAN MOVEMENT.

1. *The Nature of the Brownian Movement.*

WHEN tiny solid particles are suspended in a liquid medium, it is found that they do not remain inert but move incessantly. This phenomenon was observed by Leeuwenhoek, Stephen Gray and Buffon, but owing to lack of sufficiently powerful microscopes these investigators failed to recognise the nature of the particles and ascribed the motion to the presence of animalculæ. In 1828, Brown,[1] from a study of pollen dust in water, was able to prove that no vital action was concerned in the matter.

It was not until forty years later, however, that any detailed investigation of the Brownian movement was made. In 1868, Dancer[2] showed that particles of gamboge suspended in water were in continual motion; and he also observed that the smallest oil-globules in milk had a Brownian movement, a fact which proves that the suspended material need not necessarily be a solid. About the same time, Jevons[3] extended our knowledge of the phenomenon to a considerable extent. He proved that the motion is independent of the material of the particles but depends upon their size; that the motion appears to be related to the stability of the suspension used; and that certain impurities in the water of the system have considerable influence upon the movement. From the effects observed when electrolytes were added to the water, he was led to suggest that the stability of the particles in suspension was due to electrical charges upon them.

The following are the main characteristics of the Brownian movement. It is shown only by particles having a diameter

[1] Brown, *Phil. Mag.*, 1828, **4**, 101; 1829, **6**, 161; 1830, **8**, 41.
[2] Dancer, *Trans. Manch. Phil. Soc.*, **1868**, 162; **1870**, 37, 82.
[3] Jevons, *ibid.*, **1870**, 78.

Digitized by Google

of not more than 0·01 mm. In the case of such particles, the movement takes the form of an oscillation about a fixed centre; and the particle maintains approximately the same position while vibrating hither and thither at random through small distances. When the particles are much smaller, as in the case of some gold sols for example, the motion is much more violent and the particles dart hither and thither in the liquid, often travelling through comparatively long distances and showing no sign of returning to their original positions. In fact, there is such a difference between the behaviours of large and small particles that Zsigmondy[1] at first regarded the motions in the two cases as being entirely different in their origin. It is now known, however, that the two types of vibration are essentially the same.

The chemical character of the particles and of the pure liquid in which they float appears to be without influence upon the Brownian movement.[2] On the other hand, the viscosity of the liquid has a very marked effect upon the motion of the suspended particles; for it has been found that the amplitude of vibration of any fixed size of particles is inversely proportional to the viscosity of the liquid. As was stated above, the amplitude of vibration increases as the size of the particles is diminished.

As to the influence of external factors upon the movement, it appears to be almost negligible. Whether the liquid is kept absolutely still or subjected to irregular mechanical vibration from the outside, the motion of the particles seems to be exactly the same.[3] There is no reason to suppose that convection currents in the liquid have anything to do with the phenomenon, since effects due to them are easily distinguishable from the true Brownian movement. The presence of light does not appear to be essential to the movement, for suspensions which have long been kept in the dark show the phenomenon just as actively as those which have been illuminated. Evaporation has also been removed from the list of possible causes by keeping the specimen in contact with air saturated with the liquid in which the particles are suspended; and under such

[1] Zsigmondy, *Zur Erkenntniss der Kolloide*, p. 107.
[2] Svedberg, *Zeitsch. Elektrochem.*, 1906, **12**, 853, 909.
[3] Gouy, *Journ. de Physique*, 1888, **7**, 561; *Compt. rend.*, 1889, **109**, 102.

Digitized by Google

conditions, when no evaporation takes place—or at least, where there is no change in the equilibrium of the system—the phenomenon proceeds as briskly as ever. At one time it was supposed that an alteration in the supply of heat to the system had an effect upon the Brownian movement; but more recent work seems to show that the change in vibration with alteration in temperature is due merely to the variation in the viscosity of the liquid which is thus produced. There seems to be no cessation of the movement; for Brownian motions have been observed in the case of liquid inclusions in certain rocks, in which case the process must have been maintained for an extremely long period. Magnetic fields appear to have no influence upon the motion of the particles unless these be themselves magnetic in character.[1]

One agent appears to have a profound effect upon the Brownian motion. When an electrolyte is added to the suspension of fine particles, the usual result is a retardation of the motion and, in many cases, its complete cessation.*

2. *Measurements of the Brownian Movement.*

In order to establish the laws governing the Brownian movement, it was necessary to obtain direct measurements of the motions exhibited by the suspended particles; and various methods have been devised to accomplish this task.

The earlier investigators appear to have followed the movement of particles by means of a micrometric glass scale, the time being taken by a watch. Perrin and his colleagues[2] employed a microscope with a camera lucida and noted the position of a particular particle every thirty seconds. The microscope being vertical in their experiments, this method gives only the horizontal displacements of the particles; since the vertical displacement escapes the instrument. Under these conditions, particles could sometimes be followed for half an

[1] Gouy, *loc. cit.*; Bache and Meade, *Proc. Amer. Phil. Soc.*, 1894, 33.

[2] Perrin, *Les Atomes*, 1913, p. 173; *Atoms*, 1916, p. 122; Chaudesaigues, *Compt. rend.*, 1908, **147**, 1044; Dabrowski, *ibid.*, 1909, **149**, 477.

* Svedberg believes that the Brownian movement is independent of electrical charges; but the evidence of the effect of electrolytes is so extensive that it can hardly be brushed aside merely on this account. See Perrin, *Les Atomes*, 1913, p. 121, footnote, or *Atoms*, 1916, p. 85, footnote.

Digitized by Google

hour without passing out of view. Fig. 25 shows the tracks of particles determined by this method.

By combining the ultramicroscope and the cinematograph, Henri[1] overcame the difficulties of direct observation and produced permanent results from which the personal equation is absent. An exposure was made every twentieth of a second and the exposure itself was only $\frac{1}{3\frac{1}{2}0}$ second. By means of

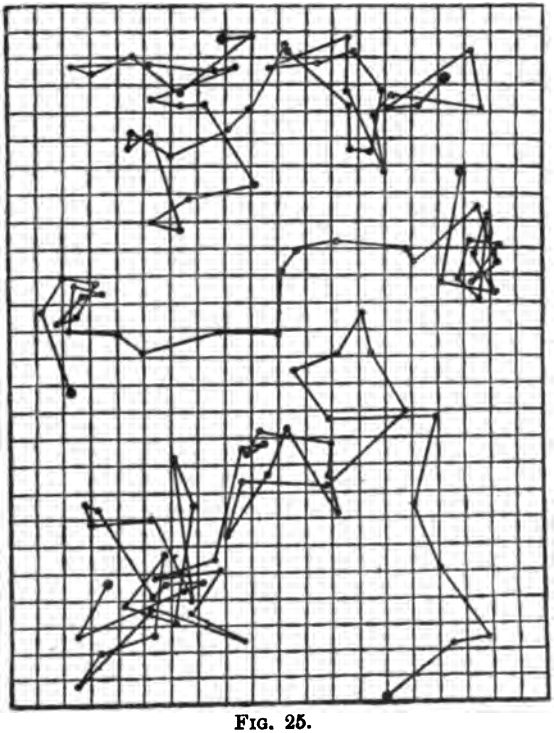


FIG. 25.

From Lewis's "A System of Physical Chemistry".

these photographs, the paths of the particles could be traced out comparatively simply.

A third method has been devised by Svedberg.[2] By passing a colloidal solution slowly through the field of the ultramicroscope, he imparted to all the particles a uniform velocity of known magnitude. If the particles had no proper motion of

[1] Henri, *Bull. Soc. fr. phys.*, 1908, **4**, 45, 61.

[2] Svedberg, *Zeitsch. Elektrochem.*, 1906, **12**, 853, 909; *Zeitsch. physikal. Chem.*, 1910, **71**, 571.

Digitized by Google

their own, the effect on a photographic plate in the ultramicroscope would have taken the form of a series of straight lines parallel to the direction of flow of the liquid. If, however, the particles were moving independently of the liquid stream, any motion at right angles to the stream would be reproduced on the plate; and their tracks would be wavy lines instead of straight ones. The amplitudes of the waves in a line furnishes a measure of the movement of a given particle, since the rate of flow is known. In this way, from the wavy line on the plate it is possible to reconstruct the proper motion of the particle.

3. *The Kinetic Theory and the Brownian Movement.*

It was surmised by the earlier investigators of the Brownian movement that the phenomenon was explicable on the assumption that collisions were taking place between the suspended particles and the molecules of the liquid in which they floated. Ramsay appears to have been the first to carry the matter into the stage of quantitative results. From his observations he calculated[1] that a particle weighing $2{\cdot}8 \times 10^{-12}$ grms. would have a velocity of $1{\cdot}4 \times 10^{-4}$ cms. per second; and he suggested, further, that the underlying cause of the action of electrolytes on the motion might be sought in a breakdown of large associations of water-molecules, so that the impacts of the water-aggregates would be feebler when an electrolyte was present in solution.

Even without bringing quantitative measurements to bear, there is enough evidence to show that the kinetic hypothesis is a probable one. It will be recalled that the nature of the Brownian movement varies with the size of the particles in suspension: tiny particles move quite at random, whilst heavier masses tend to oscillate around fixed points and do not fly hither and thither throughout the liquid. This behaviour is exactly what might be predicted from the kinetic hypothesis. A massive particle will move only slightly under the collision of a lighter solvent molecule; and since the impacts of solvent molecules take place on all sides of the particle, it will tend to move approximately about a fixed position. The lighter par-

[1] Ramsay, *Proc.*, 1892, 7, 17.

Digitized by Google

ticles, on the other hand, since their masses are more comparable with those of the solvent molecules, will suffer great displacements as a result of collisions; and hence their motions will be much more violent and haphazard than those of the heavier particles.

The theoretical investigation of the motion of particles in a colloidal solution has been carried out by Einstein,[1] Langevin[2] and Smoluchowski.[3] The two former authors arrived independently at the following equation:—

$$A^2 = \frac{R.T}{N} \times \frac{\tau}{3\pi r\eta}$$

in which A and τ are respectively the amplitude and oscillation period of a particle of radius r; η is the viscosity of the fluid in which the particles are suspended; N is the number of molecules in a gramme-molecule of substance; R is the constant of the gas equation; and T is the temperature on the absolute scale. The equation deduced by Smoluchowski differs from this only in the insertion of a numerical fraction on the right-hand side of Einstein's expression.

In order to test the accuracy of the equation, various methods may be employed. In the first place, by inserting the values for all the factors on the right-hand side and then examining the movement under the conditions thus determined, some idea may be gained of the general applicability of the expression. The following figures[4] give a selection of the results which have been obtained in this way:—

Radius in cms. × 10^5.	Viscosity.	Temp. Cent.	Amplitude of vibrations in cms./sec. × 10^5.	
			Calculated.	Observed.
8·0	0·0107	18°	6·5	5·0
6·5	0·01	21°	7·5	27·0
5·0	0·011	17°	36·0	124·0
4·5	0·01	21°	9·0	33·0
2·0	0·01	21°	13·6	38·0
0·5	0·01?	20°?	227·5	280·0

[1] Einstein, *Ann. Physik.*, 1905, **17**, 549; 1906, **19**, 371.
[2] Langevin, *Compt. rend.*, 1909, **149**, 549.
[3] Smoluchowski, *Ann. Physik.*, 1906, **21**, 756.
[4] Burton, *Physical Properties of Colloidal Solutions*, 1916, p. 75.

Digitized by Google

A comparison of the calculated and observed values shows that they lie within the same order of magnitude, though numerically they are considerably at variance.

Other methods of testing the equation depend upon varying separately each of the values for (*a*) the oscillation period; (*b*) the radii of the particles; (*c*) the viscosity of the liquid; and (*d*) the temperature, while keeping all the other factors constant. Observations of the movement will then show whether or not it varies in accordance with the equation.

(*a*) Measurements of the oscillation period have been made by Chaudesaigues.[1] He employed fifty grains of gamboge having a diameter of $2{\cdot}13 \times 10^{-5}$ cms., and by making observations at regular intervals of thirty seconds he obtained a series of relationships between the time and the movement of the particles. Now, according to Einstein's equation, the oscillation period varies as the square root of the time, so that by taking the ratio between the distance moved and the time in the first thirty seconds as a standard and calculating the other values upon this basis it is possible to see whether the equation holds good or not. The following are the results :—

Time in seconds	30	60	90	120
Observed movement in microns .	6·7	9·3	11·8	13·95
Calculated movement in microns	6·7	9·46	11·6	13·4

It will be seen from the figures that the agreement between theory and observation is extraordinarily close.

(*b*) The influence of the radii of particles upon their velocity has also been examined by Chaudesaigues.[1] Working with gamboge particles having radii of $4{\cdot}5 \times 10^{-5}$ cms. and $2{\cdot}13 \times 10^{-5}$ cms., he found that when other conditions were constant the velocities of the particles were inversely proportional to the radii, as is required by Einstein's equation.

(*c*) If the Einstein expression be correct, the velocity of the particles should vary inversely as the square of the viscosity. This has been tested by Chaudesaigues[1] and by Seddig[2] and found to be correct.

(*d*) When the influence of temperature upon the vibration is considered it must be borne in mind that change in temperature produces an alteration in the viscosity of the liquid of

[1] Chaudesaigues, *Compt. rend.*, 1908, **147**, 1044.
[2] Seddig, *Physikal. Zeitsch.*, 1908, **9**, 465.

Digitized by Google

the system; so that both factors must be taken into account. If all the other parts of the expression are kept constant, the following relationship obviously holds good:—

$$A = \sqrt{\frac{T}{\eta}}$$

Utilising a fine suspension of cinnabar in water, Seddig[1] tested the accuracy of this equation and found that even over wide ranges of temperature there was but little deviation in the value of the square root, the greatest departure from the theoretical value being about 6 per cent.

It thus appears that the equation represents with considerable accuracy the relationships between the various factors concerned in the Brownian movement. In fact, considering that the theory assumes that the particles are rigid spheres, which they certainly are not, the agreement between theory and practice is extraordinarily good.

4. *The Brownian Movement in Gases.*

In 1881, Bodoszewski made certain observations of Brownian movements in a gas-filled space; but he attempted no quantitative measurements of the displacements. More than a quarter of a century elapsed before Ehrenhaft[2] recorded values for the displacements of particles; and even then there was no attempt made to measure the sizes of the particles, so that nothing definite could be inferred from the results.

The pioneer in the quantitative study of the movement was de Broglie,[3] who utilised, in the first instance, the dust particles arising from an arc or spark passing between metallic electrodes and examined their behaviour by illuminating them with a beam of light at right angles to the line of vision. Later, he employed minute droplets of water condensed upon particles of tobacco smoke.

By placing the particles between two metal plates oppositely charged with electricity, de Broglie found that the particles were separable into three sets: those moving towards the positive plate, those remaining unaffected and those travelling towards the negative plate.

[1] Seddig, *Physikal. Zeitsch.*, 1908, **9**, 465.
[2] Ehrenhaft, *Ann. Physik.*, 1906, **21**, 756.
[3] de Broglie, *Compt. rend.*, 1908, **146**, II., 1175; 1909, **148**, 1316.

Digitized by Google

Later work was carried out by Millikan using minute drops of oil, which are more suitable in many ways.[1]

It appears that the absolute displacements of a particle in air and in hydrogen are respectively eight and fifteen times as great as they are in water; and by reducing the pressure of the gas, the displacements can be raised even to 200 times that of the displacement in water. Further, the measurements in the case of gases are free from the difficulties involved in the case of liquids owing to the presence of factors representing the radius of the particles and the viscosity of the medium.

[1] Millikan, *The Electron*, Chapter VII.

Digitized by Google

CHAPTER XI.

PERRIN'S RESEARCHES ON THE DISTRIBUTION OF PARTICLES IN EMULSIONS.

1. *Introductory.*

AN examination of chemical phenomena suggests immediately that they represent two simultaneous changes; an alteration in the matter of the system under consideration and a modification of the distribution of energy throughout the different components of the system. Thus a complete description of the reaction between two compounds should include an account of their alteration in physical properties and also a statement of the changes which the energy of the system has suffered during the reaction.

Admitting the reality of matter, the molecular theory and the kinetic hypothesis follow as a natural course; for by means of them it is possible to describe clearly the alteration in physical properties which is the result of chemical action. Thus the view that matter is real leads almost inevitably to the devising of "mechanical models" by means of which it is possible to visualise mentally the machinery of chemical processes.

During the last quarter of the nineteenth century, however, there grew up under the leadership of Ostwald a group of chemists whose outlook was different from this. According to them, the existence of matter was a mere hypothesis which it was desirable to drop as soon as possible; and the "real" factor upon which they concentrated their attention was energy.

It requires no great power of imagination to see the lines upon which these two schools of chemical thought were bound to progress. The school of Ostwald pinned their faith to general mathematical expressions by means of which they hoped in

Digitized by Google

time to be able to classify all chemical changes under certain heads. Curiously enough, Ostwald appears to have been blind to the most obvious consequences of his main conception. If it is desirable to avoid hypotheses as far as possible, then the existence of energy itself becomes an undesirable postulate. Changes in matter we can appreciate by means of our senses; but changes in energy manifest themselves only through the modification of matter. When we measure temperature by means of a thermometer, the actual subject of our observations is the position of matter in a tube; in the measurement of electrical potential our real criterion is the displacement of matter in the form of a volt-meter needle; whilst our time-measurements also are based upon the movement of matter from one place to another. Upon these measurements, which depend upon our senses, we superimpose the hypothesis of energy; and although this hypothesis is probably a correct one, it is none the less a stage further removed from "reality" than our material measurements are. Thus Ostwald's attempt to dispense with the idea of matter and yet deal with energy is almost parallel to the effort of a man to lift himself off the ground by tugging at his own coat collar: for it seems illogical to measure energy changes by means of matter and then to imagine that the results so obtained will hold good if the idea of matter be dispensed with entirely.

The "atomic" school of chemistry, on the other hand, has gone forward from triumph to triumph during the last three-quarters of a century. In 1852, Frankland brought forward the conception of constant valency, thereby opening up a new field of application for the atomic theory of Dalton. Nine years later, Pasteur was driven by his experimental results to conclude that chemistry must widen its borders and take spatial factors into consideration. The year 1862 saw the foundation of the modern theory of chemical structure laid by Kekulé;[1] and since then the gigantic development of organic chemistry has furnished ample justification of the atomic theory. In 1867, the law of mass action in its turn drew strength from the conception of material particles at the base of chemical phenomena; and within seven years van't

[1] Couper's paper (*Phil. Mag.*, 1858, **16**, 104) failed to attract attention.

Digitized by Google

Hoff and Le Bel showed that certain properties of matter could best be accounted for by the assumption of atoms occupying definite positions in space. In 1881, van der Waals was able to account for the behaviour of highly compressed gases on the hypothesis that molecules actually had ascertainable volumes.

It is quite correct to say that a theory is "only a theory" even though it fits all the known facts; but the extraordinary developments of the Daltonian atomic theory suggest that it must have very firm foundations. At the present day it is possible to synthesise a new compound and before synthesising it to predict with accuracy its molecular weight, its composition, its chemical properties, its refractive index, its magnetic rotation, its occurrence or non-occurrence in the optically active condition and sometimes even it colour; and all this depends upon the acceptance of the atomic theory of matter. Nothing of the kind has ever been attempted, much less achieved, by the Ostwald school of chemistry; and it seems probable, to judge from some of Ostwald's writings, that he was incapable of grasping the importance of the facts which organic chemistry has brought to light.

At the beginning of the twentieth century, then, the school of molecular reality had practically carried the day; for their views found application in all branches of the science, whereas the whole field of organic chemistry seemed to be *terra incognita* to the more devout followers of Ostwald. It was evident to any impartial mind that molecular reality, if not actually proved, was at least something better than a mere hypothesis which might eventually be discredited; and it became clear that both matter and energy played a definite part in chemical changes, so that chemistry could progress only by taking into account both factors and not by attempting to ignore the influence of one of them.

In the present chapter an attempt will be made to describe some recent work tending to establish molecular reality upon a still firmer experimental basis; but before entering upon this, it may be well to indicate the exact bearing of the researches in question.

Van't Hoff's extension of the gas laws into the field of dilute solution brought the kinetic theory to bear upon a

Digitized by Google

new branch of the subject; and the experimental work of Raoult showed how wide an application could be given to the new ideas. Since the molecule of cane-sugar, with its forty-five atoms, was found by Raoult to have the same influence on osmotic pressure as the water-molecule containing only three atoms, there seemed to be no reason to assume that an increase in molecular weight, even to an indefinitely great extent, would produce deviations from the general rules governing the phenomena.

Now, up to this point, the difficulty of establishing molecular reality on a firm basis had lain in the fact that molecules cannot be experimentally observed. All that can be done is to measure indirectly the effects produced by them, as in the case of the determination of the osmotic pressure of a given solution. If visible molecules could be prepared, direct observation of their motion could be made; and thus the matter would be taken out of the field of theory and brought within the region of observation.

The next step was due to Perrin,[1] and it marks a very great advance in our knowledge in this field. Following out the train of thought indicated in the last paragraph, Perrin put the question: "Is it possible that the laws of perfect gases may be applicable even to visible particles in emulsions?" Since the gas laws are valid in the case of dilute solutions, even when the solute is of high molecular weight, is it not possible that they may be applicable also to the case of aggregations of molecules suspended in a liquid, the suspended masses being sufficiently large to permit of their movements being observed by means of the microscope? To test this, Perrin undertook his examination of the properties of emulsions with which the remainder of this chapter will deal.

2. *The Preparation of Emulsions.*

For his investigations, Perrin employed emulsions consisting of grains of mastic or gamboge suspended in water. In the case of mastic, it was found sufficient to dissolve the resin in alcohol and then add water to the solution. Gamboge, when treated with water, is dispersed into a swarm of spherical

[1] See Perrin, *The Brownian Movement and Molecular Reality*, 1910; and Perrin, *Les Atomes*, 1913; Perrin, *Atoms*, 1916.

Digitized by Google

grains of various sizes; and a similar result is obtained by using alcohol to dissolve the actual colouring matter of the pigment and then precipitating the solution by means of water, just as in the case of mastic. The emulsions thus produced were placed in a centrifuge, by means of which the grains were thrown down as a sediment, whilst a tinted liquid formed a second layer in the tube. The liquid was poured off; water was added and the grains were stirred up again; after which the mixture was once more centrifugalised. After several repetitions of this process, the supernatant liquid remained quite clear; and the material was ready for the next stage in the work.

The spherical grains obtained in this way were of very different sizes; and since it was necessary to have a homogeneous material for the purposes which Perrin had in view, means had to be employed which would sift out one set of grains from the rest according to diameter. A very lengthy and laborious process of "fractional centrifugalisation" achieved the desired result. By breaking off the centrifugal action before the whole of the suspended material had been deposited, Perrin was able to separate the particles into two fractions; and continued repetition of this process led eventually to the production of preparations suitable for his investigations. As an example of the tediousness of the method, it may be mentioned that in order to obtain a few decigrammes of a homogeneous material it was necessary to start with a kilogramme of gamboge, and the separation required several months of work.

Having in this way obtained a fraction containing grains of homogeneous size, Perrin proceeded to determine the density of these granular masses. Three methods were adopted. The first was the ordinary one for determining the density of an insoluble powder by filling a specific gravity bottle with the emulsion and then, by evaporation of the emulsion, determining the mass of the solid material. In the second method, the assumption was made that the density of the gamboge or mastic is the same, no matter what its state of aggregation. The solid residue left behind in the first method was suspended in water; potassium bromide was added until the fragments of resin neither rose nor sank in the liquid; and then the density of the solution of potassium bromide was determined

Digitized by Google

in the usual way. The third method consisted in centrifuging the grains in a solution of potassium bromide of increasing concentration until a point was reached where the action of the centrifuge failed to bring the grains either to the top or bottom of the liquid. The density of the solution was then estimated as usual. In dealing with the same set of grains, the three methods gave closely concordant results: for example, in the case of some gamboge particles the densities determined by the three methods were respectively 1·942, 1·94 and 1·95.

In addition to the density it is essential to determine the volume of the grains; and here, again, Perrin employed three different methods in order to provide a control upon the accuracy of his results. In the first place, he made a direct measurement of the diameters of the grains. When a drop of very dilute emulsion was allowed to evaporate on a microscope slide, Perrin noticed that the grains of resin ran together under the action of capillary forces; so that when the liquid had almost entirely passed away, the grains were left in closely packed groups side by side, just as small shot lie on a tray. By counting the number of grains in a row and measuring the total length of the row, it was easy to determine the diameter of the particles; and since the error in measurement was less in the case of a long row than it would be in the case of a single particle, this method had an advantage over a direct measurement of individual particles.

The second method devised by Perrin depended upon another observation made by him. When gamboge grains are suspended in a feebly acid liquid, the particles do not adhere to one another; but when they strike the glass walls of the containing vessel they stick firmly. Thus after a few hours, all the gamboge spheres are found clinging to the surfaces of the microscope slide or the cover glass. By counting the grains on a given area at leisure the number of them in a given volume of emulsion can be found; and since the strength of the same emulsion can be established by desiccating another portion of it and weighing and measuring the volume of the residue, it is possible to determine the mass and the volume of each grain present.

Perrin's third method depends upon the application of Stokes' Law. According to Stokes, when a spherical particle

Digitized by Google

falls with a uniform motion under the influence of gravity through a fluid, its velocity can be expressed by the following equation:—

$$v = \frac{2gr^2}{9\eta}(D - d)$$

wherein v is the velocity, r is the radius of the particle, g is the gravity constant, η is the viscosity of the fluid, D is the density of the particle and d the density of the fluid. By observing the rate of descent of the particles of an emulsion within a capillary tube in a thermostat, Perrin was able to estimate the value of v; and since all the other necessary factors in the equation are already known, this permits the calculation of the radius of the spheres in the emulsion.

Here again the results of the three independent methods show a surprising agreement, as can be seen from the following figures which give the diameter in microns of the particles in the same emulsion:—

From Rows.	From Weights.	From Velocity of Fall.
0·371	0·3667	0·3675

To appreciate the extraordinarily laborious character of the experimental work, it must be borne in mind that certain of the measurements involved the counting of as many as 10,000 grains.

3. *The Theoretical Distribution of Gas Molecules in a Vertical Column.*

In order to understand the bearing of Perrin's next series of investigations it is necessary at this point to turn to the behaviour of gases, since his further researches were directed toward the discovery of a possible parallelism between gas molecules and the particles in his emulsions.

In a vertical column of air extending upwards from the surface of the earth it is evident that the pressure must diminish uniformly as we rise upward along the column; for the lower layers are suffering the pressure of all the remainder of the column and this remainder decreases regularly as the column is ascended. The law which expresses this reduction in pressure is very easy to establish.

For the sake of simplicity, consider the case of a vertical

Digitized by Google

column of gas having a cross-section of unit area and a height represented by h. The volume of the gas is obviously h. Assume that the mass of the gas in the column is m. It is evident that the ratio between the mass of the gas, m, and the volume of the gas, h, is the same as the ratio between the mass of a gramme-molecule, M, of the gas and the volume, v, which that gramme-molecule occupies under the same average pressure. From this it follows that—

$$m = \frac{h \,.\, \mathrm{M}}{v}$$

and since the force acting upon the mass m of gas and tending to draw it to the bottom of the tube is gm, where g is the gravity constant, we have as an expression of this force—

$$gm = \frac{g \,.\, h \,.\, \mathrm{M}}{v}$$

Now the same force can be expressed in terms of the pressures at the top and bottom of the column, *i.e.*, by $p - p'$, where p is the pressure at the foot and p' the pressure at the top. Hence we may write the equation thus—

$$p - p' = \frac{g \,.\, h \,.\, \mathrm{M}}{v}$$

Since $pv = \mathrm{RT}$, the equation may be further modified by substituting for v the value RT/p, in which case it becomes—

$$p - p' = \frac{g \,.\, h \,.\, \mathrm{M} \,.\, p}{\mathrm{R} \,.\, \mathrm{T}}$$

(This assumption only holds good, of course, when there is very little difference between p and p'.)

Rearranging the equation, it takes the form—

$$p' = p\left(1 - \frac{gh\mathrm{M}}{\mathrm{RT}}\right)$$

Now inspection shows that all the factors within the bracket are constants except h, so that if h itself be made a constant, the ratio between p and p' becomes constant. In other words, if the vertical cylinder of height h be placed anywhere in the atmosphere, the ratio of the pressures at the two ends will be constant, no matter at what altitude the cylinder be situated.

Digitized by Google

Finally, since the pressure exerted by the gas is proportional to the number of molecules present in unit volume, we may substitute for p and p' the corresponding values n and n' which represent the number of molecules in unit volume of the gas at either end of the column. By this means we arrive at the final form of the equation :—

$$\frac{n'}{n} = 1 - \frac{ghM}{RT}$$

which will hold good for any particular gas of molecular weight M.

Let us now apply this equation to determine the relations between the numbers of molecules in unit volume at different altitudes; and to simplify printing, the equation may be written in the form $n'/n = kh$. Suppose that the number of molecules per unit volume at the sea-level is n; then the number at the height h will be khn; and at the height $2h$ it will be k^2h^2n, since for the height $2h$ the number of molecules per unit volume, n'', is given by the equation—

$$n'' = n'kh = nkh \,.\, kh = nk^2h^2$$

so that the general expression for the relation between the number of molecules per unit volume and the height at which they are placed is—

$$n' = n(kh)^x$$

where x equals the difference in levels divided by h. We thus arrive at the final deduction that *a linear increase in the height of the column corresponds to a geometrical decrease in the number of particles at the top*, since kh has a value less than unity.

The expression deduced above may be applied to determine the relative heights of two columns of different gases which show equal degrees of rarefaction. The ratio between the pressures p and p' will remain the same provided that the value of M . h is kept constant. Thus if M, the molecular weight of the gas, be diminished, the value of h, the height of the column, must be increased to a corresponding extent. For example, if hydrogen and oxygen be compared, since the molecular weights of these gases stand in the ratio of

Digitized by Google

1 : 16, it is clear that to produce an equal degree of rarefaction in the two gases the hydrogen column must be sixteen times as high as the column of oxygen.

It is now necessary to turn to emulsions again and see what modifications are necessary in the equations deduced above in order that they may be applicable to this particular case—always provided that they are applicable at all.

In the first place, the force attracting the particles to the bottom of the column in the case of an emulsion is not the same as that which acts in gases, since the particles are partly supported by the liquid in which they float. The actual force at work upon them is thus not gm but is less than this by mgd/D, where d is the density of the liquid and D is the density of the particle. Secondly, for the gramme-molecular weight of the gas molecule it is necessary to substitute the value Nm, in which m is the mass of the particle and N is the number of molecules in one gramme-molecule of a gas. Making these substitutions, the fundamental equation becomes—

$$\frac{n'}{n} = 1 - \frac{m \cdot N}{R \cdot T}\left(1 - \frac{d}{D}\right)gh$$

If, on examination by experimental methods, the distribution of granules in an emulsion agrees with this formula, then it is evident that the particles in that emulsion conform to the gas laws; and, since the granules in the emulsion can be seen by the eye, they will form a visible mechanism corresponding to the molecular machine which hitherto we have had to take on trust. Not only so, but since all the factors in the above equation are measurable directly with the exception of N, it will be possible by observation to arrive at the value of this constant.

4. *The Observation of Emulsions.*

In order to determine the distribution of particles in an emulsion, two possible methods suggest themselves. The most obvious of the two is to place the emulsion in a vertical cell, wait till the preliminary disturbance is over and the particles have settled down into their normal distribution, and then examine the arrangement of the grains through

Digitized by Google

a horizontal microscope. In this way, the emulsion presents an appearance like that shown in Fig. 26. It will be seen from this picture that the grains are much more densely packed at the foot of the vessel than they are at the top,

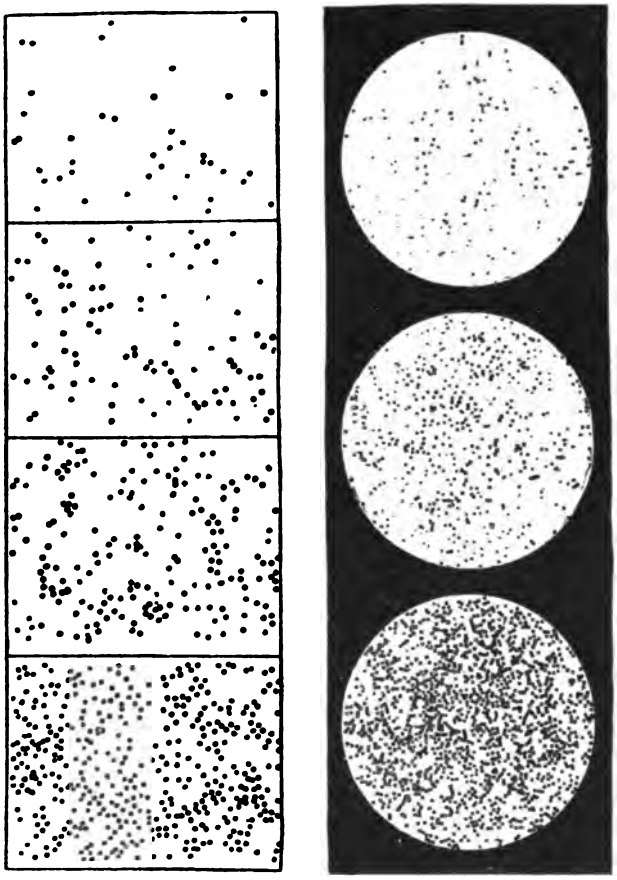


FIG. 26.

From Lewis's "A System of Physical Chemistry".

and that between these two positions there is a uniform diminution in the concentration of the granules.

This method of observation, however, is not the best possible, as it is difficult to count the grains under these circumstances. The scheme actually employed by Perrin can be made clear by an examination of Fig. 27. A drop

Digitized by Google

of the emulsion is placed in the hollow of a bored-out disc which rests on the microscope slide. The upper surface of the emulsion is made plane by means of a cover glass. All the joins in the glass part of the apparatus are covered with paraffin wax to prevent evaporation of the emulsion. A high-power microscope having a slight depth of field is placed as shown in the figure. Owing to the shallow depth of field, the microscope shows only a single layer of grains at any particular level, those immediately above and below this level being out of focus. In this way, by raising or lowering the objective it is possible to examine successively a series of horizontal layers of the emulsion; and by restricting the field by means of a diaphragm, Perrin was able to count the number of grains visible at any moment in the layer under examination. The application of instantaneous photo-

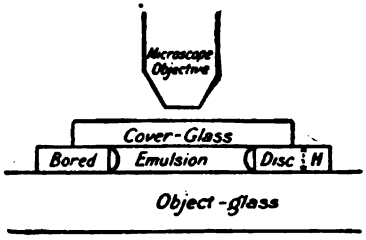


FIG. 27.

From Lewis's "A System of Physical Chemistry".

graphy is also possible; but the experimental difficulties are considerable. Fig. 26 shows the state of affairs in three different layers of the same emulsion, the lower layers obviously containing higher concentrations of granules than the upper ones. The distances between the layers can be read directly from the micrometer head of the microscope's fine-adjustment screw.

5. *Comparison between Theory and Practice in Emulsions.*

From what has already been said, it is clear that the first test of the similarity between gases and emulsions will be provided by an examination of the distribution of the granules at various depths. If the depths are in arithmetical progression whilst the numbers of granules in the layers lie in geometrical progression, then the parallelism between emulsions and gases

Digitized by Google

may be taken as *prima facie* established. It will be sufficient to give two series of Perrin's results.

Using a gamboge emulsion in which the grains had a diameter of 0·212 micron and taking readings by means of the microscope at four different levels thirty microns apart from each other (at 5, 35, 65 and 95 microns above the bottom of the vessel), Perrin found that concentrations were proportional to the following series of numbers:—

Level in microns . . .	0	30	60	90
Concentration in layer . .	100	47	22·6	12
Geometrical progression .	100	48	23	11·1

The lowest row of figures shows a series of numbers in true geometrical progression; and it can be seen that the difference between this and the series of concentrations observed is remarkably slight.

Using mastic grains having a diameter of 0·52 micron, the concentrations in four layers six microns apart were found to be—

Level in microns . . .	0	6	12	18
Concentration in layer . .	1880	940	530	305
Geometrical progression .	1880	995	528	280

Though the results in this case are not so good as in the last, there can be no doubt as to the nature of the general relation between the altitude of the layer and the concentration of the granules in it. *It is exactly the same relation as that which holds good in gases.*

Perrin and his collaborators have subjected the matter to the most stringent tests by varying the material of the grains, the density and nature of the liquid and the temperature of the emulsion; but in all cases the experimental results are in close accord with the theory.

6. *Conclusion.*

By the methods which have been described on the foregoing pages, Perrin established an almost perfect parallelism between the movement of visible grains in an emulsion and the invisible agitation of molecules in a gas; but in order to appreciate the closeness of the parallel it is necessary to mention here a point which will be more fully dealt with in the next chapter. From

Digitized by Google

his experimental results, Perrin was enabled to calculate the value of Avogadro's constant N, the number of molecules contained in one gramme-molecule of a material. Values for this constant can also be obtained from a study of the properties of gases, as well as in other ways; and in general the figures found were ranged between 60×10^{22} and 70×10^{22}. The value calculated by Perrin from the distribution of grains in a column of emulsion is $68{\cdot}3 \times 10^{22}$, which is obviously a very close approximation to that gained from investigations of gases; and this constitutes yet another resemblance between emulsion-particles and gas-molecules.

An emulsion, then, may be considered to be "a miniature ponderable atmosphere" composed of particles which are gigantic in comparison with the gas-molecules making up our own atmosphere but which nevertheless conform to the same general laws.

Finally, Perrin's work appears to place beyond doubt the accuracy of the kinetic theory of the Brownian movement. The movements of the grains in his emulsions correspond on the one hand to the vibrations of molecules in a gas, and on the other side to the flights of colloidal particles undergoing Brownian movements. His work does not allow us to *see* the actual movements of molecules; but it permits us to observe directly and to measure accurately the factors concerned in a motion which takes its rise in molecular agitation and which conforms to similar laws. The agreement between the kinetic theory and the practical results is very much closer than there was any reason to expect; and Perrin's work seems to have removed the last doubts of most investigators as to the accuracy of the molecular theory of matter.

Digitized by Google

CHAPTER XII.

AVOGADRO'S CONSTANT AND MOLECULAR DIMENSIONS.

1. *The Factor N.*

In 1811, Avogadro put forward the hypothesis that under the same conditions of temperature and pressure, equal volumes of two gases contain equal numbers of molecules. It should be noted that in this unqualified form, the hypothesis is obviously incorrect. For example, if the temperature and pressure chosen be approximate to those at which carbon dioxide liquefies, it is obvious that a litre of carbon dioxide under such conditions cannot contain the same number of molecules as a litre of hydrogen at the same temperature and pressure, since the latter is far removed from its critical condition and the two gases are not in comparable states. Theoretically, Avogadro's hypothesis is strictly applicable only to gases under infinitely low pressure. But since at standard temperature and pressure most gases are far removed from their critical conditions, Avogadro's hypothesis serves quite accurately enough for all practical purposes.

The acceptance of the hypothesis suggests a line of speculation. Since in 22·4 litres of a gas under standard conditions of temperature and pressure there is always the same number of molecules, whether the gas be hydrogen or chlorine or any other gas; and since, further, 22·4 litres of gas under these conditions always contains a gramme-molecule of the gas; it seems of importance to determine, if possible, what the number of the molecules is: for clearly this number is a natural constant; and, further, if it can be ascertained, it leads directly to the determination of the absolute weight of a given molecule. This figure (the number of molecules contained in a gramme-molecule of any gas) is known as Avogadro's constant and is usually indicated by the letter N.

Digitized by Google

Up to the present, more than a dozen methods have been employed to ascertain the value of Avogadro's constant; and it is impossible to enter into the details of them all in this place. Only a sketch can be given; but it will be sufficient to bring to light the diversity of the methods and the extraordinary concordance among the results which have been obtained in so many different ways.

2. *The Upper Limit of Molecular Diameter.*

If a thin, continuous sheet of any homogeneous material be prepared, it is evident that its thickness cannot be less than the diameter of one of the molecules of which it is composed; so that by measuring the thickness of the sheet it is possible to determine the superior limit of the molecular diameter.

In the case of the well-known films of translucent gold, the thickness of the leaf is found to be about one-tenth of a micron; which proves that the diameter of the gold atom cannot exceed this value and the maximum limit of the volume of the gold atom must be less than 10^{-15} c.c. This implies that the maximum possible weight of a single atom of gold is 10^{-14} grms.; and since the hydrogen atom is two hundred times lighter than the gold atom, the hydrogen atom cannot have a mass greater than $5{\cdot}0 \times 10^{-16}$ grms.

Turning to films of liquid, the most familiar are those found in soap-bubbles. The thinnest parts of these films are in the black areas which form just before the bubble bursts. By measuring the electrical resistance and by optical interference measurements, Reinold and Rucker[1] obtained values pointing to a thickness of 12×10^{-7} cms. The phenomenon is too complex to yield satisfactory values, however, apart altogether from the inhomogeneous nature of the soap film.[2]

Even thinner films can be obtained by spreading oil upon water. It will be remembered that when a piece of camphor is placed on the surface of water, the camphor darts about in all directions owing to differences in surface tension induced by the solution of the camphor in the water. By placing a trace of oil upon the water surface, this movement is inhibited, since the layer of oil has a surface tension lower than that of pure

[1] Reinold and Rucker, *Phil. Trans.*, 1886, **177**, 627.
[2] Johonnot, *Phil. Mag.*, 1899, **47**, 501.

Digitized by Google

water. Rayleigh utilised this phenomenon as a gauge of the presence of oil upon a water surface; and he determined the weight of the smallest drop of oil which, when placed upon a known surface-area of water, would prevent the camphor-movement at any part of the surface. From the experimental results he was able to prove that the thickness of the oil film on the water could not exceed two-thousandths of a micron; so that the diameters of the oil molecules could not be greater than this value.

Devaux[1] improved Rayleigh's method by using oil mixed with benzene. When the mixture is spread on the water surface, the benzene rapidly evaporates, leaving a film of oil even thinner than those obtained by Rayleigh. If powdered talc be sprinkled on the surface from a sieve and then blown across the water, it is found to accumulate at the line of demarcation of the oil film, the area of which can thus be measured with accuracy. The thickness of Devaux's oil films was found to be little more than a millimicron.

Perrin[2] observed that a 0·1 per cent. solution of fluorescein shows a uniform green fluorescence in volumes of the order of a cubic micron; so that the mass of the molecule of fluorescein is certainly less than the thousandth of the mass of a cubic micron of water. Since the molecular weight of fluorescein is 332, it is clear that the hydrogen atom weighs less than 1/332 of a cubic micron of water. This gives the approximate mass of a hydrogen molecule as less than 10^{-21} grms; and its diameter must be less than 25×10^{-8} cms.

3. *Methods Based upon the Kinetic Theory of Gases.*

Before entering upon the methods of determining molecular magnitudes by means of the kinetic theory of gases, one point must be made clear. Let it be assumed that in the gas under examination the molecules have a diameter s. Then obviously the bulk of a single molecule will be $\frac{\pi}{6} s^3$; and the total volume of the whole of the molecules in one gramme-molecule of gas will be $\frac{\pi}{6} s^3 N$, where N is Avogadro's constant and represents

[1] Devaux, *Jour. de Phys.*, 1904, 3, 450.
[2] Perrin, *Les Atomes*, 1913, p. 71; *Atoms*, 1916, p. 49.

Digitized by Google

the number of molecules contained in one gramme-molecule. Now suppose that the molecules are spherical. When they are compressed until they touch one another, they will obviously be occupying the smallest possible bulk, but this bulk will not be $\frac{\pi}{6} s^3 N$; for even when the spheres touch one another there will still be interstices between them at certain points, just as a heap of shot is a porous mass and not a solid, continuous material. Calculation shows that the true volume of the molecules alone must be less than three-fourths of the total bulk of molecules-plus-interstices. The symbol e in the expression below was termed by Clerk Maxwell the ideal coefficient of condensation—

$$e = \frac{\pi}{6} s^3 N \quad . \quad . \quad . \quad . \quad . \quad (1)$$

As was shown by Maxwell,[1] the length of the mean free path of a molecule in a given gas under standard conditions of temperature and pressure can be expressed by

$$l = \frac{22{,}400}{\pi s^2 N \sqrt{2}} \quad . \quad . \quad . \quad . \quad (2)$$

where N is Avogadro's constant,[2] l is the length of the mean free path and s is the diameter of one molecule.

The value of l can be obtained from measurements of the viscosities of gases in the following manner. From the kinetic theory it can be shown that the viscosity of a gas is related to the mean free path of the molecules thus:—

$$\eta = \tfrac{1}{3}\delta l c \quad . \quad . \quad . \quad . \quad . \quad (3)$$

where η is the viscosity of the gas, l is the mean free path, δ is the gaseous density, and c is the velocity of the molecules. Now in the other expression $pv = \frac{1}{3}mnc^2$, also deduced from the kinetic theory, we may choose v as unit volume and write δ instead of the factor mn, since the mass of a gramme-molecule is proportional to the density of the gas. This gives the

[1] Maxwell, *Collected Papers*, 2, 348.

[2] In his paper, Maxwell uses N to represent the number of molecules in 1 c.c. of gas. The factor 22,400 is introduced above to make N into Avogadro's constant.

Digitized by Google

expression $p = \frac{1}{3}\delta c^2$; from which by rearrangement we obtain—

$$c = \sqrt{\frac{3p}{\delta}} \quad . \quad . \quad . \quad . \quad (4)$$

Substituting this value of c in equation (3) we find—

$$\eta = \tfrac{1}{3}\delta l \sqrt{\frac{3p}{\delta}}$$

whence

$$l = \eta\sqrt{\frac{3}{p\delta}} \quad . \quad . \quad . \quad . \quad (5)$$

The value of $\mathfrak{e}$ can be determined approximately as follows: According to the Clausius-Mossotti theory of dielectrics,[1] the relation between the dielectric constant, ϵ, of a material and the value of $\mathfrak{e}$ for that substance is given by—

$$\epsilon = \frac{1 + 2\mathfrak{e}}{1 - \mathfrak{e}}$$

whence it follows that

$$\mathfrak{e} = \frac{\epsilon - 1}{\epsilon + 2}$$

According to the electromagnetic theory of light, if n be the refractive index of the substance for light of very long wavelength, then $\epsilon = n^2$; so that by introducing this value into the equation and dividing throughout by the density, d, of the substance, we find—

$$\frac{\mathfrak{e}}{d} = \frac{n^2 - 1}{n^2 + 2} \times \frac{1}{d}$$

Here n and d are experimentally measurable; and the value of $\mathfrak{e}$ can be obtained. Further, the fraction $\frac{\mathfrak{e}}{d}$ denotes the volume actually occupied by the molecules of one gramme of the substance.

Going back to equations (1) and (2) and multiplying them together, it is found that—

$$22{,}400s = 6\mathfrak{e}l\sqrt{2}$$

and it is evident that since both $\mathfrak{e}$ and l can be ascertained by

[1] Clausius, *Gesammelte Abhandlungen*, 2, 135.

Digitized by Google

methods shown above, the value of s, the molecular diameter, can be calculated. Knowing s, the value of N may be obtained by substitution in either (1) or (2).

Various calculations of molecular magnitudes[1] have been made, using determinations of the viscosities of gases as a basis. The following figures are given by Rankine—

Element	Cl	Br	I	A	Kr	X
Molecular radius $\times 10^{-8}$ cms. . .	1·60	1·71	1·88	1·28	1·88	1·53

Another method, which gives approximate values for the diameters of molecules is furnished by the application of van der Waals' equation—

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

in which the factor b represents four times the true volume of the gas molecules.* The value of b can be obtained from compressibility measurements.

Van der Waals' equation can be utilised also in another form. By applying it to the critical conditions and treating it as a cubic equation with three equal roots, the following expressions are obtained for the critical pressure P_K and the critical temperature T_K :—

$$P_K = \frac{a}{27b^2} \qquad T_K = \frac{8a}{27Rb}$$

Dividing one equation by the other, we obtain—

$$\frac{RT_K}{P_K} = 8b$$

from which it is evident that the fraction RT_K/P_K gives a measure of the relative sizes of molecules of different gases.[2]

In order to understand the next method of determining Avogadro's constant, it is necessary to bear in mind the fact

[1] Jeans, *Phil. Mag.*, 1904, **8**, 692; Sutherland, *ibid.*, 1910, **19**, 25; Cuthbertson, *ibid.*, 1911, **21**, 69; Rankine, *ibid*, 1915, **29**, 552; *Proc. Roy. Soc.*, 1910, **83**, 516.

[2] Van der Waals, *Proc. K. Akad. Wetensch. Amsterdam*, 1914, **16**, 880.

* D. Berthelot inserts a further correction in Boyle's Law, making the equation

$$\left(P + \frac{a}{TV^2}\right)(V - b) = RT.$$

Digitized by Google

that a gas when in the neighbourhood of the critical state exhibits a peculiar opalescence which is termed the critical opalescence. It has been shown by Smoluchowski[1] that this phenomenon is due to the presence of dense swarms of molecules in the material, the existence of these swarms being rendered possible by the fact that near the critical point (where the compressibility of the gas is very great) it is possible for the density of the gas to differ markedly in closely contiguous regions. It has been shown theoretically[2] that when a ray of light strikes a small transparent particle of fixed volume placed in a medium of different refrangibility, the intensity of the light deviated from the particle at right angles to its original path is inversely proportional to the fourth power of the wave-length of the incident light and directly proportional to the square of the volume of the particle and to the square of the relative difference in refractive index between the particle and the medium in which it floats. Now, in the case of the density fluctuations in a vapour, the relative difference in refractive index is proportional to the mean variation in density of the material, a factor which Smoluchowski has calculated. Inserting the value found by him, the intensity i of the light diffused by 1 c.c. of the material at right angles to the incident rays is given by—

$$i = \frac{\pi^2}{18} \times \frac{1}{\lambda^4} \times \frac{RT}{N} \times (\mu_o^2 - 1)^2 \times (\mu_o^2 + 2)^2 \times \frac{1}{-v_o \cdot \frac{\partial p}{\partial v_o}}$$

where μ_o is the mean refractive index of the fluid for light of wave-length λ in vacuo, v_o is the specific volume of the liquid and $\frac{\partial p}{\partial v_o}$ represents its isothermal compressibility. Since all the factors in this expression are experimentally ascertainable with the exception of N, the equation furnishes a means of determining Avogadro's constant.

Actual experiments on ethylene made by Onnes and Keeson have shown that the method is a practical one; and the result of their work led to the value $N = 75 \times 10^{22}$, the experimental error being about 15 per cent.

[1] Smoluchowski, *Acad. Sci. Cracow*, December, 1907.
[2] Rayleigh, *Phil. Mag.*, 1881, **41**, 86; Lorenz, *Œuvres*, I., 496.

Digitized by Google

As was pointed out by Rayleigh, somewhat similar considerations apply to the blue light which comes to us from the sky on a clear day. Here it is assumed that the nitrogen and oxygen molecules act as diffracting centres. Measurements made by Brillouin[1] lead to the value $N = 60 \times 10^{22}$, but these results are probably not without sources of error.

4. *The Determination of N from Properties of Emulsions.* In the last chapter, some account was given of Perrin's researches upon the distribution of particles in emulsions; and it was pointed out that he used the equation—

$$\frac{n'}{n} = 1 - \frac{mN}{RT} \cdot \left(1 - \frac{d}{D}\right) gh$$

in which n and n' are the numbers of particles observed in layers separated by a height h; m is the mass of the particle; D and d are respectively the densities of the particle and of the liquid in which it floats; R and T are the gas equation constants; g is the gravity constant; and N is Avogadro's constant. It is evident that when Perrin had determined the relative numbers of particles in two layers at different altitudes in the emulsion, he had obtained a means of measuring N, since all the other factors in the equation were known. The results obtained in this way ranged between 65×10^{22} and 72×10^{22}, the average being $68{\cdot}3 \times 10^{22}$. From this it follows that the mass of the hydrogen atom is in the neighbourhood of $1{\cdot}47 \times 10^{-24}$ grammes.

Perrin[2] has utilised direct observation of the Brownian movement in order to determine Avogadro's constant by a fresh method. According to Einstein's theory, if the Brownian movement be completely irregular, then the mean square of the horizontal displacement of a particle in an emulsion should be directly proportional to the time occupied in the displacement. The same relation holds good, of course, for the horizontal component of the displacement, which we may term x during the time t; from which it follows that x^2/t is a constant. Now Einstein has shown that on his assumptions, the coefficient of diffusion D for an emulsion is equal to half this constant, so

[1] See Perrin, *Les Atomes*, 1913, p. 197; *Atoms*, 1916, p. 139.
[2] Perrin, *Les Atomes*, 1913, pp. 160 ff.; *Atoms*, 1916, pp. 111, ff.

Digitized by Google

that $D = x^2/2t$. But since Stokes' Law holds good for emulsions, then, if it be assumed that, at equal concentrations, grains and molecules produce equal osmotic pressures, the following equation holds good:—

$$D = \frac{R.T}{N} \cdot \frac{1}{6\pi r\eta}$$

where r is the radius of the grains and η is the viscosity of the liquid in which they float. Equating the two values of D, we obtain the expression—

$$\frac{x^2}{t} = \frac{R.T}{N} \cdot \frac{1}{3\pi r\eta}$$

Thus if the viscosity of the liquid and the radius of the particles be known, it is possible to determine N by means of observations of the displacements of the particles in unit times. This Perrin carried out by means of the camera lucida, making an enormous number of measurements with various grains of different sizes and materials, and employing liquids of different viscosities. The values for N obtained in these investigations varied between 64×10^{22} and 80×10^{22}, the average being in the neighbourhood of 70×10^{22}. Using an emulsion of mercury in water, Zangger[1] arrived at the values—

$$N = 63{\cdot}2 \times 10^{22},\ 62{\cdot}4 \times 10^{22} \text{ and } 61{\cdot}9 \times 10^{22}$$

Emulsions supplied Perrin with yet another method[2] of evaluating N. According to Einstein's theory, the Brownian movement of rotation—*i.e.*, the spin imparted to the particles by molecular collisions—obeys the law expressed in the equation

$$\frac{A^2}{t} = \frac{R.T}{N} \cdot \frac{1}{4\pi r^3\eta}$$

where A^2 stands for the third of the mean square of the angle of rotation in time t and the other symbols have the same meaning as before.

In order to observe the rotational movement of particles in emulsions two conditions have to be fulfilled. In the first place, the particles must be comparatively large; and secondly, they must have markings on their surfaces which will enable their

[1] Zangger, *Zeitsch. Chem. Ind. Kolloide*, 1911, **9**, 216.
[2] Perrin, *Les Atomes*, 1913, p. 177; *Atoms*, 1916, p. 124.

Digitized by Google

rotation to be measured. These conditions were fulfilled by certain grains of gamboge and mastic which Perrin prepared by running pure water from a spout underneath an alcoholic solution of the resin; and then allowing the two liquids to diffuse into each other. On the border region, spherical granules up to 50μ in diameter were formed; and these granules had certain inclusions in them which enabled their velocity of rotation to be determined with comparative ease. Owing to the mass of grains of this size, it was necessary to use a solution of urea in which to suspend them, for in water they sank to the bottom.

Observations of the rotational movement of these granules and the application of the formula given above led Perrin to the value $N = 65 \times 10^{22}$.

A final method employed by Perrin[1] will serve to conclude this survey of emulsion properties. Desiring to measure directly the rate of diffusion of the grains in an emulsion, he took advantage of the fact that when suspended in glycerine, the granules adhere to the walls of the vessel as soon as they touch the glass. They are thus left in position and can be counted at leisure.

The theory of the method is as follows: Suppose that a uniform gamboge emulsion containing n grains per unit volume is enclosed by a vertical glass partition. The partition captures every grain which is driven against it by the Brownian movement, so that the emulsion tends to become steadily weaker and weaker. If $\mathfrak{N}$ be the number of grains collected on unit surface of the glass, it is evident that this quantity will increase steadily; and that it can be used as a gauge of the coefficient of diffusion. Let X^2 be the mean square (equal to $2Dt$) of the displacement of the particles during the time t which has elapsed since the beginning of the experiment. It may be assumed without much error that each particle has undergone the displacement X either towards the wall of the vessel or in the opposite direction. The number of grains stopped by unit surface of the wall during the time t is, on this assumption—

$$\mathfrak{N} = \frac{n \cdot X}{2}$$

[1] Perrin, *Les Atomes*, 1913, p. 181; *Atom*, 1916, p. 129.

Digitized by Google

Substituting Dt for X and squaring both sides of the equation we obtain—

$$\mathfrak{R}^2 = \frac{n^2 . Dt}{2}$$

whence, by rearranging—

$$D = \frac{2\mathfrak{R}^2}{n^2 . t}$$

This gives an expression in which all the factors except D can be determined; and when this has been found by calculation, the substitution of it in the equation—

$$D = \frac{R . T}{N} . \frac{1}{6\pi r\eta}$$

permits the evaluation of N.

Using gamboge grains of radius $0{\cdot}52\mu$ in an emulsion containing $7{\cdot}9 \times 10^8$ grains per c.c. of glycerine, observations were made photographically twice daily for several days on the same area of the glass wall of the vessel. The examination of the negatives and the counting of the grains captured during each period led to the value $D = 2{\cdot}3 \times 10^{11}$. When this value is substituted in the last equation above, then N is found to be within 3 per cent. of 69×10^{22}.

Taking the most probable values from his measurements, Perrin [1] gives the following results:—

From vertical distribution of grains	$N = 68{\cdot}2 \times 10^{22}$
From Brownian movement of translation	$N = 68{\cdot}8 \times 10^{22}$
From Brownian movement of rotation	$N = 65 \times 10^{22}$
From diffusion measurements	$N = 69 \times 10^{22}$

It must be confessed that the agreements between results obtained in so many different ways are almost amazing, in view of the difficulties which the experimental work presents at every turn. The application of the kinetic theory to emulsions has been vindicated in an almost unanticipated fashion by Perrin's investigations; and his work has placed the problem of molecular reality upon a very firm footing, since no other hypothesis serves to explain the phenomena.

5. *The Determination of N from Radiation Phenomena.*

A full account of the method of evaluating N by means of investigations of radiation would necessitate a discussion of

[1] Perrin, *Les Atomes*, 1913, p. 188; *Atoms*, 1916, p. 182.

Digitized by Google

Planck's quantum theory, which cannot be given here. Space precludes more than the merest outline of the reasoning which is employed.

Imagine a cell so enclosed that neither heat nor light can pass from the exterior to the interior or *vice versa*. In the course of time, every point in the interior of this cell will be in thermal equilibrium with every other point, so that no matter where a thermometer is placed within the cell it will always register the same temperature. Consideration will show that under these circumstances if a diaphragm be placed anywhere within the cell, the quantity of light or heat passing through the diaphragm in one direction will be exactly the same as that which passes through it in the opposite direction.

Further, if a small aperture were pierced in the wall of the cell, any light entering through this hole would be so dispersed by successive reflections from the walls of the cell that it would fail to illumine the interior. An example of this in practice is to be found in the case of a very high temperature furnace, in which the eye can appreciate nothing owing to the blurring of details. No beam of light which can be thrown into the furnace will reveal anything, because the light beam does not return again to the aperture through which it entered.

This aperture in the cell, then, behaves like a section of a totally black body, because it fails to re-emit the light which falls upon it from the outside, just as a black body absorbs all incident rays.

The state of stationary equilibrium of light or thermal vibrations does not depend upon the presence of matter in the cell; for a thermometer placed in a completely evacuated isothermal compartment would show exactly the same unchangeable temperature.

Now imagine that the isothermal cell be filled with sodium vapour. Since sodium vapour at a high temperature emits the vibration known as the D-line of the spectrum, it is evident that the sodium atoms are in a state of vibration of a definite period. The isothermal cell under these conditions will therefore contain light which is in equilibrium with the atoms. The matter is made clearer if it be assumed that the atoms contain resonators with a short period of oscillation and

Digitized by Google

that these resonators, in their vibrations, take up from and give out to the light exactly equal quantities of energy.

But since the whole interior of the isothermal cell is in a state of equilibrium, it follows that in this equilibrium must be included the vibrations of the atoms in space. Thus on the one hand a sodium atom is in thermal equilibrium with the light vibration and on the other it is in thermal equilibrium with the other sodium atoms in the vessel; so that the mean energy of oscillation must be the same as if it were solely sustained by the impacts of the gaseous molecules; for otherwise a kind of perpetual motion might be possible.

If ordinary conditions are supposed to prevail within the isothermal cell, it is clear that the kinetic energy of oscillation of the gaseous particles can be deduced from the usual equations—

$$PV = RT = \frac{1}{3}mnc^2$$

from which it can be shown that the mean kinetic energy of oscillation has the value $\frac{3R \cdot T}{2N}$. Since this expression contains nothing relating to the period of vibration, it is evident that, *under the assumptions we have made*, the wave-length of the light in the isothermal cell should have no relation to the "density" of the light present, this density factor being a measure of the conditions in the cell.

In actual practice, however, it is found that the density of the light varies inversely as the fourth power of the wave-length of the light; and the equation of Planck—

$$w_\lambda = \frac{8\pi}{\lambda^4} \cdot E \quad . \quad . \quad . \quad . \quad (A)$$

apparently expresses the state of affairs correctly. Here ω_λ is the density of the light for a given wave-length λ; and E is the mean energy of the oscillators. Now, when the wave-length becomes very small, according to this equation, the radiation should increase—which is exactly the reverse of the experimental results. By experiment it is found that the radiation density becomes infinitely small for very short wave-lengths; which implies that when the frequency is very high

Digitized by Google

the mean energy of the oscillators must also become extremely small.

This conflict between theory and practice arises from the fact that it has been assumed tacitly throughout that the energy of the oscillators varies *continuously*. If, instead, it be postulated that the energy alters *discontinuously*—*i.e.*, that there are "grains of energy" just as there are atoms of matter —a mathematical treatment of the problem again becomes possible. Each oscillator then has to cope with n "grains of energy" (or quanta, as Planck terms them) where n is always a whole number. The value E of this "grain of energy" depends upon the oscillation-frequency, ν, of the oscillator and may be expressed as $h\nu$, where h is a universal constant known as Planck's constant.

Making the assumptions of Planck, it can be shown that in order to attain statical equilibrium between the radiant energy and the kinetic energy of the molecules within the isothermal cell the following relationship must hold good:—

$$E = ch\left(e^{\frac{N}{R}\cdot\frac{ch}{\lambda T}} - 1\right)^{-1}$$

in which N is Avogadro's constant, T is the absolute temperature, λ is the wave-length of light ($1/\nu$) and c is the velocity of light. By modifying this in accordance with equation (A) above, we obtain—

$$w_\lambda = \frac{8\pi ch}{\lambda^5}\left(e^{\frac{N}{R}\cdot\frac{ch}{\lambda T}} - 1\right)^{-1}$$

Now, in this equation, everything is measurable except Avogadro's constant and Planck's constant h; and these can be calculated from the results of two experiments in which either T or λ is varied.

In this way it has been found that $h = 6{\cdot}2 \times 10^{-27}$ electrostatic units; whilst $N = 64 \times 10^{22}$.

6. *The Determination of N from Charges on Gaseous Ions.*

The principle of this method is easy to understand, though the experimental work demands the utmost refinement. The following will suffice to make the *modus operandi* clear:—

The current required to deposit a gramme-atom of silver

Digitized by Google

from the solution of a silver salt is easily determined. This current evidently represents the charge on a monovalent ion multiplied by the number of molecules in the gramme-molecule of the silver salt used; so that it can be denoted by Ne where e is the charge carried by one monovalent ion. If, now, the value of e can be ascertained by some other method, it is clear that the factor N can be determined.

Various methods of determining e have been employed;[1] and it will be sufficient merely to indicate the outlines of two of them. By means of Wilson's dust-counter,[2] it is possible to produce a cloud of minute drops, each of which is gathered round an ion which has been produced in the vapour previous to condensation. By utilising Stokes' Law, the radius of the drops can be calculated; and therefore the weight of a drop is known. From this, the number of drops per c.c. of gas may be found; for we can determine the weight of the cloud contained in one c.c. The total charge on one c.c. of the gas can be determined by an electrometer. Dividing the total charge by the number of drops, we obtain the charge on a drop. In the case in which the charge on the ion was greater than e, it was found always to be a multiple of e, no fractional values being obtained. This seems to establish the corpuscular nature of electricity.

More exact methods were evolved later. The main difficulty in the earlier methods lay in the fact that Stokes' Law is not accurate when applied to the case in point; but in Millikan's experiments oil drops from a vaporiser were employed, which agreed better with the requirements of Stokes' equation. The use of oil excluded errors due to evaporation which were a drawback in the case of water drops; and the diameter of the oil drops was much greater than that of the water drops. Millikan employed the method suggested by H. A. Wilson, in which the charged drops are placed under the influence of a known electrical field. If v be the velocity of the cloud falling under the action of gravity and v' be the velocity of fall when subjected to the influence of an electrical field of intensity X, then for a drop of mass m and

[1] See Townsend, *Electricity in Gases*, Chapter VII.; Millikan, *The Electron*.

[2] C. T. R. Wilson, *Phil. Trans.*, 1897, A, 189, 265; 1899, A, 192, 403.

Digitized by Google

charge e, the gravitational force acting on the drop is mg and the electrical force is Xe. From this it follows that—

$$\frac{v}{v'} = \frac{mg}{mg + Xe}$$

and since all the values except e are known, the charge can be found.

In Millikan's experiments, the apparatus was so refined that a single oil drop could be kept in the field of view for a number of hours at a time, the gravitational pull being in this case counteracted by the action of the electrical field.

The value of the charge e was found to be $4{\cdot}9 \times 10^{10}$, which gives the figure $N = 59 \times 10^{22}$ for Avogadro's constant by the method outlined above.

7. *Methods Depending upon Radioactive Properties.*

The methods of applying the phenomena of radioactivity to the problem of Avogadro's constant are in principle very similar to those mentioned in the foregoing section, since they depend upon the establishment of the value of e, the charge carried by a gaseous ion. In the present case, however, the gaseous ion is furnished by radioactive sources and takes the form of the α-particle.

It is obvious that two figures have to be determined: the number of α-particles concerned in the experiment and the total charge which they carry. The methods of counting depend either upon the scintillations produced by the impact of the particles on a zinc sulphide screen or upon the fact that the passage of an α-particle ionises a gas through which the particle travels.

When an α-particle traverses any gas, the collisions with the particle ionise the gas and make it capable of conducting electricity. Thus by forcing the particle to pass through a gas at low pressure and between electrodes charged nearly to sparking potential, an electrometer in the circuit will be affected by the ionisation although the passage of the α-particle alone would not suffice to influence the instrument. By using a string galvanometer,* Rutherford and Geiger were able to

* The effect is so great that even an ordinary electrometer can be used.

Digitized by Google

detect and count the particles passing through this apparatus.[1] In this way[2] they found that the number of α-particles expelled per second by one gramme of pure radium is $3{\cdot}4 \times 10^{10}$.

Regener[3] determined the number of α-particles by allowing them to impinge upon a zinc sulphide screen and counting the scintillations thus produced. His method is simpler than the electrical one; but it gives no proof that a scintillation is produced by a single α-particle. The control of the electrical method, however, enables us to say that this is the case.

Knowing the number of α-particles entering a receiver in a given time, it is only necessary to measure the charge accumulated in the receiver in order to determine the charge on each particle. This was done by Rutherford and Geiger[4] by means of a special apparatus which avoided error due to the presence of β and other rays.

The values obtained by these investigators for the charge on the α-particle was $9{\cdot}3 \times 10^{10}$; and since the particle carries two charges, this gives $e = 4{\cdot}65 \times 10^{10}$. The value of N calculated from this datum is 62×10^{22}.

The radioactive substances provide a second method whereby N may be ascertained. Boltwood and Rutherford[5] measured the volume of helium liberated per annum by one gramme of radium (in equilibrium with its disintegration products) and found it to be 156 cubic mm. This corresponds to 39 cubic mm. per gramme of pure radium per annum. Now, since there are $(60 \times 60 \times 24 \times 365)$ seconds in the year and since in each second there are $3{\cdot}4 \times 10^{10}$ α-particles ejected by the gramme of radium, it is clear that 39 cubic mm. of helium contains $(60 \times 60 \times 24 \times 365 \times 3{\cdot}4 \times 10^{10})$ helium atoms; from which it follows that 22·4 litres of helium contain—

$$\frac{60 \times 60 \times 24 \times 365 \times 3{\cdot}4 \times 10^{10} \times 22{,}400}{0{\cdot}039} = 62 \times 10^{22}.$$

[1] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, A, **81**, 141; *Physikal. Zeitsch.*, 1909, **10**, 1.

[2] For full experimental details see Rutherford, *Radioactive Substances and their Radiations*, 1913, p. 129.

[3] Regener, *Verh. d. deutsch. Phys. Ges.*, 1908, **19**, 78, 351.

[4] Rutherford and Geiger, *Proc. Roy. Soc.*, 1908, A, **81**, 162.

[5] Boltwood and Rutherford, *Phil. Mag.*, 1911, **22**, 586.

Digitized by Google

Thus this method yields $N = 62 \times 10^{22}$ for Avogadro's constant.

The loss of the α-particle involves the breakdown of the radium atom in which it takes its origin; and this change furnishes yet another means of determining N. From the rate of decay of radium, it can be calculated that of N radium atoms, the number which disintegrate per second is $N \times 1{\cdot}09 \times 10^{-11}$. This number must be equal to the number of α-particles ejected per second by one gramme-atom (226·4 grms.) of radium. From the figures given above, this number is $226{\cdot}4 \times 3{\cdot}4 \times 10^{10}$. Therefore—

$$N = \frac{226{\cdot}4 \times 3{\cdot}4 \times 10^{10}}{1{\cdot}09 \times 10^{-11}}$$

This gives the value of N as about 71×10^{22}.

Perrin[1] has suggested a method of determining N which is based upon the conversion of the kinetic energy of the α-particle into heat and the estimation of N from the heat emitted by radium. His method, since it takes into consideration only four series of α-particles instead of the full total of five, leads to a result which is probably too low, N = 60.

8. *The Distances of Atoms in Crystals.*

Hitherto in this chapter, attention has been concentrated upon molecules existing in the gaseous or liquid condition; but for the sake of completeness it may be well to give some information with regard to the relations in crystalline substances.[2]

In the structure of a crystal, the atoms are believed to be regularly arranged in a series of parallel planes, the whole system making up what is termed a *space lattice*. In the space lattice, the environment about every point is the same as that about every other point in the system.

In Fig. 28, the lines PQ, RS and TV represent the edges of three parallel planes containing atoms in a crystal. The heavy lines AB and CG represent a pair of incident X-rays travelling as shown by the arrows; and the line FX represents

[1] Perrin, *Les Atomes*, 1913, p. 288; *Atoms*, 1916, p. 203.

[2] For full information on this subject see Sir W. H. Bragg, *X-rays and Crystal Structure*, and W. L. Bragg, *Science Progress*, 1921, **16**, 45.

Digitized by Google

the path of rays reflected from atoms at F and B respectively. Produce CF to G. The point G is obviously the image of B in the plane RS. Draw BD from B perpendicular to CG. Then in the figure FB = FG; and the angle ABP = the angle DBG.

Now consider the distances travelled by the X-rays passing to X from A and C. In the one case, the path is AB + BX; in the other case it is CF + FB + BX. Cancelling out the common part BX and substituting CD for AB and FG for FB, the difference between the two paths is clearly DG, which may be expressed as $2d \sin \theta$.

Suppose that the wave-length of the X-ray used in the experiment is λ. Then if the value $2d \sin \theta$ is exactly equivalent to λ, the ray from F will reinforce the ray from B, both being precisely in the same phase. The same will hold good generally, provided that—

$$n\lambda = 2d \sin \theta$$

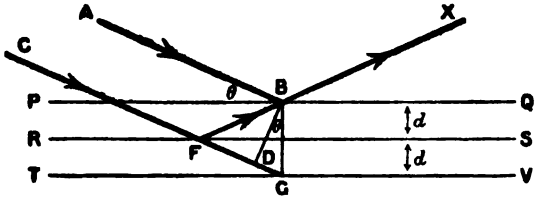


FIG. 28.

If, on the other hand, the distance DG (*i.e.*, the difference in length of path of the two rays) is not an exact multiple of the wave-length of the rays, then interference between the vibrations will take place and the combined effect of the two rays will be weaker than in the previous case.

By means of Bragg's X-ray spectrometer, it is possible to determine the wave-length, λ, of the X-ray employed and also to measure the glancing angle θ which secures the reinforcement of one wave by the other.

Let us assume that these measurements have been made in the three primary planes of a crystal in which the planes are separated by the distances d_1, d_2 and d_3 according to the direction in which we make the measurements. (In the case of the cubic crystal, obviously, $d_1 = d_2 = d_3$.) From these determinations, it is possible to establish not only the form of

Digitized by Google

the tiny parallelopiped containing the diffracting centre but also its volume, since $d = \lambda/2 \sin \theta$ and $d_1 \times d_2 \times d_3 =$ the volume of the parallelopiped.

The following table[1] shows the relationships between the distances separating atoms of metal and halogen in a series of crystals having the same structure as potassium chloride:—

	Na.	K.	Rb.
F . . .	2·39	2·73	—
Cl . . .	2·81	3·13	3·28
Br . . .	2·97	3·28	3·44
I . . .	3·23	3·52	3·66

The distances are expressed in Ångström units (1 Å.U = 10^{-8} cms.).

It will be seen that when chlorine is replaced by bromine or bromine by iodine, the distances between the atomic centres are increased by approximately the same value throughout the series of compounds; and the same holds good when potassium is substituted for sodium or rubidium for potassium. Similar relationships appear to exist in other series of compounds. Thus the substitution of sulphur for oxygen increases the intra-atomic distance in a number of compounds; and, curiously enough, the value of this increase is the same as that which results from the replacement of fluorine by chlorine. Thus in two adjacent groups of the Periodic Table a certain parallelism is to be found.

8. *Conclusion.*

In the foregoing sections of this chapter, an outline has been given of some of the methods by means of which it is possible to evaluate Avogadro's constant; and from this survey, two points emerge with clearness. In the first place, the problem is one which is approachable from many sides and which can be attacked by methods differing from each other not only in experimental details but in fundamental principles. Secondly, the results obtained by all these different methods show a concordance which is nothing less than surprising. The table given by Perrin[2] brings this out most strikingly:—

[1] W. L. Bragg, *Science Progress*, 1921, **16**, 45.

[2] Perrin, *Les Atomes*, 1913, p. 289; *Atoms*, 1916, p. 206 (modified).

Digitized by Google

Phenomena observed.		$N/10^{22}$.
Viscosity of gases		62
Brownian movement	Distribution of grains	68·3
	Displacements	68·8
	Rotations	65
	Diffusion	69
Critical opalescence		75
The blue of the sky		60?
The black body spectrum		64
Charged drops in a gas		60·62
Radioactivity	Charges produced	62·5
	Helium liberated	64
	Radium disintegrated	71
	Energy radiated	60?

It may fairly be said that the reality of molecules is definitely established by this wonderful series of concordances; for if molecular reality be rejected, it would be hard to devise any new simple hypothesis which would serve to account for the results obtained in so many different fields of research.

But apart altogether from the problem of the structure of matter, the subjects dealt with in the present chapter suggest something. As Perrin[1] points out, even if the atomic theory be eliminated, none the less the relationships between the various phenomena which have been established above remain firm. "For instance, by eliminating the molecular factor in the equations for the black body spectrum and the Brownian movement of diffusion, we arrive at an expression which will enable us to predict the rate of diffusion of spheres of one micron in diameter through water at ordinary temperatures, provided that we have made measurements of the intensity of yellow light emitted from the mouth of a furnace containing molten iron. Consequently, the physicist, by observing the furnace, will be able to discover any error in the microscopic investigations of another observer engaged in the examination of an emulsion."

The most accurate determination of Avogadro's constant appears to be that of Millikan,[2] *viz.*, $N = 60{\cdot}62 \times 10^{22}$ with an error of $\pm\ 0{\cdot}012 \times 10^{22}$. By assuming this value for N, it is possible to calculate the mass of any atom which may be

[1] Perrin, *Les Atomes*, 1913, p. 290; *Atoms*, 1916, p. 207.
[2] Millikan, *Physikal. Zeitsch.*, 1913, **14**, 796.

Digitized by Google

required. For example, since the hydrogen gramme-molecule weighs two grammes and contains $60{\cdot}62 \times 10^{22}$ molecules, the actual weight of a single hydrogen atom must be—

$$W = \frac{1}{60{\cdot}62 \times 10^{22}} \text{ grms.}$$

The weights of other atoms are obtained by multiplying this value by the atomic weight of the element in question.

Digitized by Google

CHAPTER XIII.

ADSORPTION.

1. *Sorption, Absorption and Adsorption.*

It was shown by Chappuis[1] in 1881 that charcoal has the power of taking up gases with which it is placed in contact; and that by this process an equilibrium is set up, the quantity of the gas taken up by the charcoal being dependent upon the pressure of the gas. Later work[1] has confirmed this observation. At first sight, the phenomenon appears to be similar to those which are classed under Henry's Law; but closer examination proves that the two cases are not exactly alike. The following figures will serve to show the difference. They refer to the case of charcoal and carbon dioxide at 0° C. The pressure, P, of the gas is given in millimetres of mercury; x represents the concentration of the gas in the charcoal; and if Henry's Law were obeyed, obviously x/P should be constant.

P.	x.	$\frac{x}{P}$.	$\frac{x}{\sqrt[3]{P}}$.
4·1	0·38	0.092	0·24
25·1	0·77	0·026	0·26
137·4	0·45	0·010	0·26
416·4	2·02	0·004	0·27
858·6	2·48	0·003	0·26

The figures show clearly that the quantity of carbon dioxide taken up by the charcoal is not proportional to the pressure of the gas, as Henry's Law requires, but is actually related to the cube root of the gaseous pressure; for the figures in the last column are practically constant.

[1] Homfray, *Proc. Roy. Soc.*, 1910, A, **84**, 99; Titoff, *Zeitsch. physikal. Chem.*, 1910, **74**, 641; see also Williams, *Proc. Roy. Soc. Edin.*, 1919, **96**, 287, 298.

Digitized by Google

This deviation from Henry's Law goes to prove that in this case the process is not one of solution, since that law holds good even in the region of solid solutions. The most obvious explanation of the phenomenon is arrived at if it be assumed that we have to do with a "surface effect" and that the charcoal has the power of condensing the gas upon its surface in some way.

This hypothesis is considerably strengthened by the results of further investigations.[1] In studying the behaviour of hydrogen in contact with charcoal, McBain found that the process took place in two stages. In the first stage there is a rapid imbibition of the hydrogen, which is followed by a slower process of the same kind. The explanation of this appears to be that the first stage represents the rapid condensation of the hydrogen upon the surface of the charcoal, whilst the later stage corresponds to the slow diffusion of the gas into the pores of the charcoal structure.

It is convenient to be able to distinguish between the phenomena; and adopting McBain's nomenclature, we may speak of the surface effect as *adsorption* and the diffusion into the charcoal pores as *absorption*; whilst to the joint effect of the two the name *sorption* may be given.

With absorption we need not deal here. The remainder of the chapter will be devoted to a consideration of the phenomena of adsorption.

2. *The Surface Factor.*

From what has been said above, it is evident that in adsorption phenomena the exposed surface of the adsorbing material plays a prominent part; and at this stage it may be well to deal with one or two points which bear upon this field.

The first matter of importance is the rapidity with which the surface of a material is increased by repeated subdivision. Imagine a cube, each side of which is a metre long. The total superficies of the cube will be 6 sq. metres. If the cube be now divided into a series of smaller cubes, each having a side 1 cm. in length, there will be a million of such cubes,

[1] McBain, *Phil. Mag.*, 1909, **18**, 916; *Zeitsch. physikal. Chem.*, 1909, **68**, 471; see also Davis, *Trans.*, 1907, **91**, 1666.

Digitized by Google

each of which will have a superficies of 6 sq. cms.; so that the total superficies will be 600 sq. metres. Thus, owing to the exposure of fresh surfaces, the superficies has been increased one hundred times, although the volume remains constant.

This suggests that the surface development in any material might be gauged by the ratio between the volume of the material present and the surface which it exposes; and Wo. Ostwald[1] suggested the name *specific surface* to denote this relationship in any particular case:—

$$\frac{\text{Total superficies}}{\text{Total volume}} = \text{Specific surface}$$

Now, in order to divide any material, energy is required; and when the end-products of the division are very tiny* (as in the case of a liquid split up into minute globules) the energy is stored up in the form of *surface energy*. The surface energy may be represented as the product of the surface area and the surface tension of the material in question.

Thus in colloidal solutions, where the state of division is extremely fine, it is clear that we shall have to take into consideration both the specific surface and the surface energy. But these factors are not the only ones which require examination. As has been made clear in a previous chapter, the particles in a colloidal solution carry electrical charges; and these charges will exercise some influence upon the behaviour of the colloid. Now it is well known that the presence of electrical charges upon a contractile surface produces an increase in the area of the surface, owing to the charges repelling each other and thus tending to move as far apart as possible. The mercury in a capillary electrometer furnishes a familiar example of this phenomenon. In the case of a charged colloid, therefore, it might be expected that the presence of an electrical charge upon the surface would act against the surface tension of the material and produce, if possible, an increase in the area of the surface of the particles.

[1] Wo. Ostwald, *Grundriss d. Kolloidchemie*, 1911, p. 29.

* Unless the specific surface is at least 10,000 the surface energy is so small as to be negligible for practical purposes.

Digitized by Google

Further light is thrown upon the question of surface phenomena when the case of solutions is considered. Every free liquid surface tends to diminish its energy as far as possible. For example, a small drop of mercury will assume the spherical form because in the sphere the ratio of volume to surface is the greatest possible; so that by rearranging itself into a sphere, the mercury reduces its surface and concurrently its surface energy.

In the case of a solution, the liquid may diminish its energy in two separate ways. In the first place, it may behave like mercury and reduce its surface as far as possible by contraction. Secondly, it may suffer a reduction in surface tension by altering the concentration of the solution in the surface layer at the expense of the remaining solution. Thus we may expect to find that the concentration of solute is different in the surface layer (surface concentration) than it is in the remainder of the liquid (volume concentration).

The relationship connecting concentration and surface tension has been derived in various ways,[1] of which the following seems the simplest. Let w be the surface area of a solution which contains one gramme-molecule of the solute in excess of the concentration in the main bulk of the solution; and let σ be the surface tension. Assume that a very small quantity of solute x enters the surface from the solution and reduces the surface tension by $d\sigma$. The energy corresponding to this is $wd\sigma$: and this quantity of energy must obviously be equal to that which is required to remove the same quantity of solute x from the solution. This latter quantity of energy is obviously the energy required to overcome the osmotic pressure produced in the solution by the given quantity of solute x. Let v be the volume of the solution which contains unit weight of solute and let dp be the difference between the osmotic pressure before and after the removal of the solute quantity x; then the energy employed is vdp. Since the two quantities of energy are equal, and opposite in sign, then

$$wd\sigma + vdp = 0$$

[1] Gibbs, *Trans. Connecticut Academy*, 1876, **3**, 439; J. J. Thomson, *Applications of Dynamics to Physics and Chemistry*, 1888, p. 190; Freundlich, *Zeitsch. physikal. Chem.*, 1907, **57**, 385; Milner, *Phil. Mag.*, 1907, **13**, 96.

Digitized by Google

Now, if the solute be supposed to be undissociated and the solution be a dilute one, the gas laws will apply to it and we can write RT/p instead of v, which yields the following equation:—

$$\frac{d\sigma}{dp} = -\frac{RT}{wp}$$

Since the osmotic pressure p is directly proportional to the concentration, c, in the solution, we can substitute c for p in the equation, thus obtaining the expression—

$$\frac{d\sigma}{dc} = -\frac{RT}{cw}$$

Now, since w represents the surface which contains one gramme-molecule of the solute in excess of the solute contained in the main bulk of the solution, the excess of solute, u, in unit surface is $1/w$. Substituting this value in the last equation we get the result—

$$u = -\frac{c}{RT} \cdot \frac{d\sigma}{dc}$$

From this equation it is evident that if σ is increased with increase in concentration, u is negative, *i.e.*, the proportion of solute will diminish in the surface layer and increase in the main body of the solution (negative adsorption). Conversely, if σ diminishes with increase of concentration, u is a positive quantity and the proportion of solute will increase in the surface layer (positive adsorption). The latter is the more common of the two phenomena.

If the equation is to be applicable in the case of electrolytes in solution, van't Hoff's factor i must be introduced, making the expression—

$$u = -\frac{c}{iRT} \cdot \frac{d\sigma}{dc}$$

Since no assumption has been made with regard to the nature of the surface, the formula should be applicable to the boundaries between any two materials, whether they be solids, liquids or gases.*

As is frequently the case with general formulæ, the equation

* Excluding, of course, such cases as two miscible liquids or two gases, where there is no boundary surface.

Digitized by Google

deduced above holds good qualitatively; but does not appear to represent the results actually obtained by experiment; for in experimental processes many factors intervene to complicate the problem.

The most striking of these factors is the difference found between what are termed the "static" and "dynamic" surface tensions of certain liquids. When surface tension is determined by measuring the rise of liquid in a capillary tube, the weight of a hanging drop or the curvature of a liquid surface, it is clear that the surface in question is "static" at the time of measurement; but if the surface tension be ascertained from oscillating jets, or oscillating drops, there is a continual change in the surface. In the case of a pure liquid this has little influence; but when solutions are under examination, the change in the surface concentration influences dynamic methods of determination and usually leads to the result being lower than that obtained by statical methods, as the following figures[1] show:—

	Surface Tension.	
	Dynamic.	Static.
Water	75	75
Sodium oleate solution	26	79
Heptylic acid solution	54	68
Sodium sulphate solution	72·6	75·6

A qualitative proof that the surface concentration differs from the concentration in the main body of the liquid was furnished by Zawidski[2] in the following way: The solution to be examined was mixed with saponin, which has great froth-producing power, and analyses were made of the percentage of solute in the bubbles of the froth and also in the non-frothing part of the liquid. The differences in concentration between the two were found to be considerable; and since the surface of the bubbles is enormous in comparison to the volume of liquid in their films, this result shows conclusively that the surface concentration cannot be the same as that of the remainder of the solution. Similar results were obtained by Benson[3] and Milner.[4]

[1] Taylor, *Chemistry of Colloids*, 1915, p. 231.
[2] Zawidski, *Zeitsch. physikal. Chem.*, 1900, **35**, 77.
[3] Benson, *J. Physical Chem.*, 1903, **7**, 532.
[4] Milner, *Phil. Mag.*, 1907, **13**, 96.

Digitized by Google

3. *The Phenomena of Adsorption.*

From what has been said in the foregoing sections, it will be clear that the boundary between two heterogeneous phases is remarkable for an unequal distribution of material. For example, when a piece of charcoal is placed in a vessel of carbon dioxide, the charcoal adsorbs the gas and the pressure of carbon dioxide at the surface of the charcoal is different from the pressure in the main body of the gas. In its most general form, adsorption may be regarded as a process whereby one material is held at the surface of another without any chemical reaction taking place between the two.

Since adsorption may be expected wherever two heterogeneous phases lie in contact with one another, the following systems suggest themselves as being capable of experimental investigation: (1) gas-solid; (2) gas-liquid; (3) liquid-solid; (4) two non-miscible liquids. Here the term "liquid" includes solutions. These various classes may best be dealt with by the examination of practical examples; so that course will be followed in the remainder of this section.

1. *Gas-Solid Systems.*—It has been found that in the case of charcoal, different gases are differently adsorbed, the adsorption being greatest in the case of easily liquefiable gases, as the following figures[1] show:—

Volume of Gases Adsorbed by 1 *Vol. of Charcoal at* 12° *C. and* 724 *mm.*

Ammonia	90	Carbon monoxide	9·42
Hydrogen sulphide	65	Nitrogen	6·50
Sulphur dioxide	55	Hydrogen	1·25

The relationship between adsorptive power and heat of adsorption is shown in the following table:—

Gas.	Volume Adsorbed.	Heat of Adsorption.
Ammonia	178	494
Hydrogen chloride	166	274
Sulphur dioxide	165	168
Nitrous oxide	99	169
Carbon dioxide	97	158

The figures[2] represent the volumes of the gases adsorbed

[1] Saussure, *Gilbert's Annalen*, 1814, **47**, 2, 13.

[2] Favre, *Compt. rend.*, 1854, **39**, 729; *Ann. chim. phys.*, 1874, **1**, 209.

Digitized by Google

by 1 c.c. of charcoal at ordinary temperatures and the heats of adsorption in calories per gramme of gas.

As might be expected on theoretical grounds, a rise in temperature reduces[1] the adsorptive power of charcoal.

Gas.	Volume Adsorbed at − 185° C.	Volume Adsorbed at 0° C.
Hydrogen	85	4
Nitrogen	155	15
Oxygen	250	18
Argon	175	12
Helium	15	2

Owing to the great differences in the volumes adsorbed at low temperatures, it is possible to utilise adsorption as a means of separating the inert gases from the rest of the constituents of the atmosphere. In the adsorption of gaseous mixtures, however, the relations are not quite so simple; since the equilibrium has to include all the gases present, and the relative quantities of each adsorbed will be dependent upon the partial pressure.

The conditions of equilibrium between a gas and an adsorbent solid are simply expressed in the equation—

$$\frac{x}{m} = ap^{\frac{1}{n}}$$

where x is the amount of gas adsorbed, m is the quantity of adsorbent material, p is the pressure of the gas in the space above the adsorbent, and a and n are constants for a given gas and a given solid.

Since x/m represents the concentration, C_1, of the gas on the adsorbent material and $C_2 = 1/p$ represents the concentration of the gas above the adsorbent, the equation can be written as below, where y is substituted for $1/n$:—

$$\frac{C_1}{C_2^{\,y}} = \text{constant}$$

Here, if y be made equal to unity, the expression becomes the same as that of Henry's Law. In the case of adsorption, n is greater than unity; but it is interesting to note that Henry's Law evidently represents the extreme case of the phenomenon.

[1] Dewar, *Ann. chim. phys.*, 1904, 3, 5.

Digitized by Google

For the purposes of calculation, it is simpler to use the logarithmic equivalent of the general equation, taking logarithms of both sides, the expression becomes—

$$\log x - \log m = \frac{\log p}{n} + \log a$$

in which the variables are $\log x$ and $\log p$. When $\log x$ and $\log C$ are used as ordinate and abscissa respectively, the curve expressing the adsorption phenomena takes the form of a straight line.

2. *Gas-Liquid Systems.*—In this case, the liquid may be either a pure liquid or a solution; but since the latter case is a complicated one, it is not necessary to deal with it in this place. Mercury provides the best example of this particular branch of adsorptive phenomena, since gases are only immeasurably slightly soluble in it. From what has already been said, it will be evident that adsorption on a liquid surface will produce a lowering of the surface tension. If, therefore, the surface tension of mercury in contact with a gas be measured immediately on the admission of the gas to contact with the mercury and a second determination be made after sufficient time has elapsed to allow adsorption to become complete, any difference between the two results will indicate adsorption. The following figures are sufficient to prove that mercury does adsorb various gases :—

Gas.	Temperature.	σ (Fresh Surface).	σ (After 1 Hour).
Vacuum . . .	15°	486	486
Hydrogen . . .	21°	470	434
Oxygen	25°	478	432
Nitrogen . . .	16°	489	438
Carbon dioxide . .	19°	476	429

It will be seen that *in vacuo*, the surface tension does not alter during the hour, whereas in every other case there is a lowering of the tension after the mercury has been left in contact with the gas, which seems to prove conclusively that the mercury surface has acted as an adsorbent.

3. *Liquid-Solid Systems.*—Here again, technically, the term liquid should include both pure liquids and solutions; but

Digitized by Google

the case of solutions is the only one which has been studied exhaustively, so attention may be confined to it.

In the first place, it may be well to point out that there is experimental proof [1] of the fact that adsorption is a reversible process. When one gramme of charcoal is shaken for twenty hours with 100 c.c. of a 0·0688N solution of acetic acid in water, it was found that the strength of the acid was reduced to 0·0608N. In a second experiment, one gramme of the same charcoal was shaken for twenty hours with 50 c.c. of acetic acid solution of double the strength (0·1376N); 50 c.c. of water were then added and the mixture shaken for one hour. At the end of this, the strength of the solution was found to be 0·0606N—practically the same as in the first experiment. Thus the same equilibrium is attained in both cases, whether we begin with the acetic acid concentrated in the solution or acetic acid concentrated in the charcoal.

Now let us turn to the relations between the amount of acetic acid adsorbed at equilibrium when the initial concentrations of acetic acid in water are altered. The figures [1] below show what takes place; and the results are expressed graphically in Fig. 29. C_1 represents the concentration of acetic acid in the solution in contact with the charcoal; C_2 gives the concentration in the carbon, both values being determined after equilibrium has been attained. The figures represent millimolecules of acid per c.c. The curve is termed the *adsorption isothermal.*

C_1 = 0·0181	0·0309	0·0616	0·1259	0·2677	0·4711	0·8817	2·785
C_2 = 0·467	0·596	0·801	1·11	1·55	2·04	2·48	3·76

The results in the case of the adsorption of benzoic acid in benzene solution by means of charcoal are as follows, and are also shown graphically in Fig. 29.

C_1 = 0·0062	0·025	0·053	0·118	.
C_2 = 0·437	0·78	1·04	1·44	

Just as in the case of the gas-solid systems, it is found that the equilibria in liquid-solid systems can be expressed by the general formula—

$$\frac{x}{m} = aC^{\frac{1}{n}}$$

[1] Freundlich, *Zeitsch. physikal. Chem.*, 1906, **57**, 385.

Digitized by Google

where x is the amount of solute adsorbed, m is the quantity of the adsorbent material, C is the concentration of the solute in the liquid and a and m are constants, depending upon the system. This equation is obviously that of a parabolic curve,*

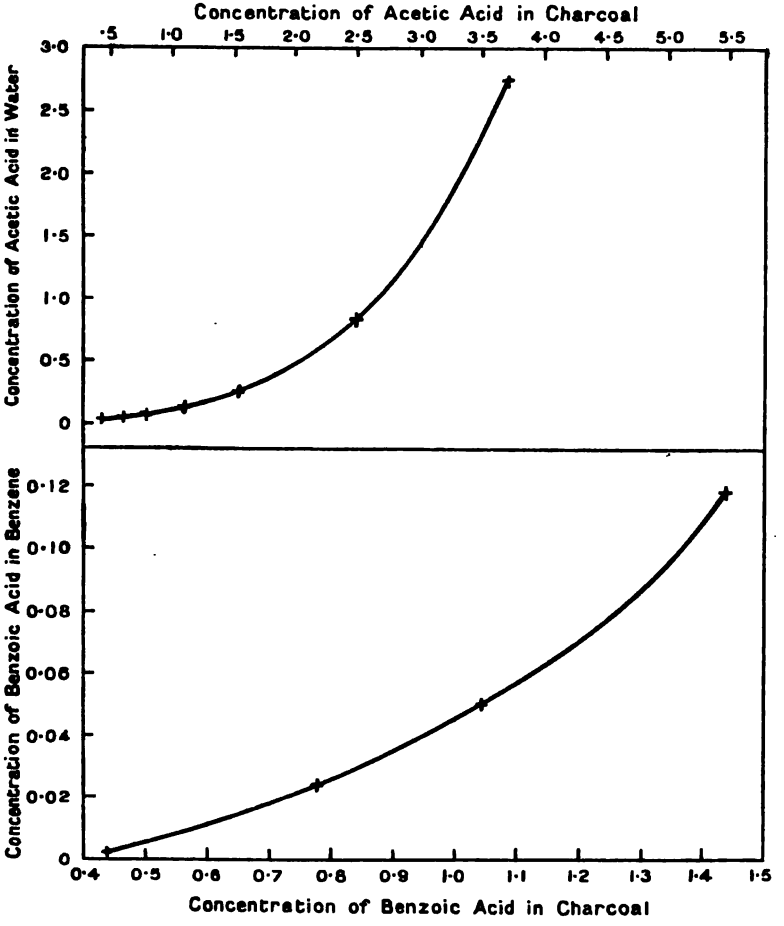

Concentration of Acetic Acid in Charcoal
·5 1·0 1·5 2·0 2·5 3·0 3·5 4·0 4·5 5·0 5·5
Concentration of Acetic Acid in Water
3·0 2·5 2·0 1·5 1·0 0·5 0
Concentration of Benzoic Acid in Benzene
0·12 0·10 0·08 0·06 0·04 0·02 0
0·4 0·5 0·6 0·7 0·8 0·9 1·0 1·1 1·2 1·3 1·4 1·5
Concentration of Benzoic Acid in Charcoal

FIG. 29.

as can be seen by inspection of Fig. 29. The value of $1/n$ varies, of course, according to the conditions of the system, as is proved by the following figures, found by Freundlich for blood

* In the case where $n = 2$, the equation can obviously be recast into the form $y^2 = 4ax$, which represents the simple conic parabola.

Digitized by Google

charcoal in presence of solutions of different substances. The solutions were aqueous except in cases where the solvent is named.

	$\frac{1}{n}$.		$\frac{1}{n}$.
Formic acid	0·451	Succinic acid	0·243
Acetic acid	0·425	Benzoic acid	0·338
Propionic acid	0·394	Chlorine	0·297
Monochloracetic acid	0·363	Bromine	0·340

	$\frac{1}{n}$.
Picric acid in alcohol	0·230
Benzoic acid in benzene	0·416
Bromine in ether	0·263

Inspection of these figures suggests at once that adsorption is not governed by chemical influences; for the value of $1/n$ varies but little throughout the series and the two halogens lie between propionic and succinic acid, which would be a very unexpected result if chemical constitution were a preponderating factor in the problem.

The fact that $1/n$ is fractional in all these cases renders it almost out of the question that the adsorbed substance is present in the charcoal in the form of a solid solution; for in this case the molecular weight of acetic acid adsorbed in charcoal would be roughly half of its molecular weight when dissolved in water, according to the usual formula for the distribution coefficient. This postulate could hardly be granted.

4. *Systems of Two Immiscible Liquids.*—In the case of gas-solid systems it was mentioned that adsorption at a mercury surface could be detected by an investigation of the surface tension. The same method can be applied in the examination of mercury in contact with other liquids; and from the results which have been obtained, there seems to be no doubt that the mercury acts as an adsorbent material. The results given below [1] were obtained by measuring the weights of the drops of water which drip from a standard orifice placed under the surface of the second liquid in the system :—

System.	Surface Tension.	Temperature.
Water-paraffin oil	48	16°
Water-benzene	32·6	20°
Water-ether	9·7	20°
Water-isobutyl alcohol	1·176	18°

[1] Taylor, *Chemistry of Colloids*, 1915, p. 258.

Digitized by Google

Lewis[1] examined the adsorptive power of the system water-paraffin oil as regards sodium glycocholate* and methyl orange. With sodium glycocholate, the following results were obtained :—

Concentration.	σ for Oil.
0·0000000	33·6
0·0000357	32·2
0·000357	28·1
0·00357	22·0
0·00643	16·8
0·0118	12·6

When compared with values calculated from the theoretical formula, these results are found to be very wide of the mark, which is probably due to the difficulties of the method employed. Other experiments were made with mercury as the adsorbent, a stream of fine drops of the metal being allowed to flow through solutions of various substances. Here again, except in isolated cases, the theory and practice were markedly at variance with each other.

4. *Adsorption and Chemical Reaction.*

It has already been pointed out that adsorption is a physical process and not a chemical reaction ; but it may be well to give some further proofs of this, as the matter is important.

One of the most striking demonstrations of the difference between adsorption and compound formation has been described by Bayliss.[2] When well-washed aluminium hydroxide is added to a dilute solution of the colloidal acid derived from the dye Congo red, the dye is taken up by the hydroxide, giving a blue product. This product is not a salt of the acid, for the salts are red in colour. It is therefore almost certainly due to the adsorption of the dye by the aluminium hydroxide. On warming a suspension of this blue material in water, the colour changes to red, showing the formation of the true aluminium salt of the acid. This change seems to establish the difference between adsorption and chemical combination in an almost indisputable way.

[1] W. C. McC. Lewis, *Phil. Mag.*, 1908, **15**, 506; *Zeitsch. physikal. Chem.*, 1910, **73**, 129.

[2] Bayliss, *Zeitsch. Chem. Ind. Kolloide*, 1908, **3**, 224.

* Glycocholic acid should not be confused with glycocoll. The former is a glycocoll derivative of cholic acid.

Digitized by Google

An indirect proof that adsorption and chemical combination are different processes is furnished by the work of Walker and Appleyard.[1] If it be assumed that in the adsorptive process we have to deal with the equilibrium between a partially dissociated solid compound and its dissociation products, then the Mass Action Law can be applied to the problem and the following equation will hold good in the liquid phase :—

$$\frac{C_1^x \times C_2^y}{C_3^z} = \text{constant}$$

where C_1 is the concentration of the adsorbent, C_2 is the concentration of adsorbed material and C_3 is the concentration of the compound formed; while x, y and z represent respectively the number of molecules of each material which are taking part in the equilibrium. Since the charcoal and the compound formed are both present in the solid state, their concentrations in the liquid phase will be constant; so that the equation becomes—

$$C_2 = \text{constant}$$

In other words, the concentration of the adsorbed material in the liquid phase will remain constant so long as both the adsorbent and the compound formed are present as solid phases. This is obviously incorrect in the case of the adsorption of acetic acid by charcoal; for, as the curves in Fig. 29 show, the concentration of the acetic acid in solution steadily increases concurrently with an increase in the total concentration of acetic acid in the system instead of remaining constant. This behaviour evidently invalidates the assumption that adsorption and compound-formation are identical processes.*

To make assurance doubly sure, however, Walker and Appleyard investigated the case of the equilibrium between solid diphenylamine and an aqueous solution of picric acid. These two compounds unite to form diphenyl-ammonium picrate which, like diphenylamine itself, is practically insoluble in water; and since the picrate partly decomposes in presence of water, yielding free diphenylamine and picric acid (which

[1] Walker and Appleyard, *Trans.*, 1896, **69**, 1334.

* In some cases, however, chemical influences enter the problem. See Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2221.

Digitized by Google

dissolves in the water), the conditions described above hold good for this equilibrium.

Making a saturated solution of picric acid in water (16 mgrs. acid per gramme of water at 40·6°), the investigators shook up 50 c.c. of this with 2 grms. diphenylamine, another 50 c.c. with 1 grm. of the base and a third 50 c.c. with 0·5 grm. of diphenylamine until equilibrium was attained. Determinations of the concentrations of picric acid in the solution and in the solid led to the following results:—

Milligrammes of Picric Acid.

In 1 grm. of Water.	In 1 grm. of Diphenylamine.
13·8	7·5
13·7	15·5
13·8	30·0

Clearly, in this case, the concentration of the picric acid in the liquid has remained constant, as was predicted from the Mass Action Law; and thus there is no resemblance between the results of this purely chemical reaction and the phenomena observed in the case of adsorption, where the concentration of the liquid phase alters.

In the course of the same investigation, Walker and Appleyard studied the interaction of picric acid and silk. By immersing fixed quantities of silk in picric acid solutions of different strengths, they were able to show that the amount of dye removed from the bath varied continuously with the concentration of the picric acid in the solution, relatively larger amounts being abstracted from weak solutions than from strong ones. It was found that the same equilibrium was attained whether the picric acid was originally in the silk or in the solution. In this case, then, the dyeing process is apparently one of pure adsorption; but it must be borne in mind that here the dye is obviously not a fast one, since it can be removed by water.

Digitized by Google

CHAPTER XIV.

SOME HYPOTHESES OF THE COLLOID STATE.

1. *Introductory.*

THE phenomena exhibited by substances in the colloidal condition are so extraordinary and so important from many points of view, both in theory and in practice, that it is not surprising to find numerous attempts made to account for the properties of colloids by means of hypotheses; and any description of colloids would be incomplete if this side of the subject were omitted entirely. At the same time, it must be admitted frankly that none of the suggestions hitherto put forward is entirely satisfactory. Nor is this surprising; for the colloid class is so ill-defined in its limits that an explanation which harmonises with the behaviour of certain colloidal materials may fail entirely when applied to others. For instance, the difference in viscosity between suspensoid and emulsoid colloids is one of the most difficult points of all to account for; and yet it is one of the most obvious phenomena in the colloid field.

In selecting examples of the hypotheses which have been proposed from time to time, the main object kept in view has been to bring out clearly the difference in the standpoints from which various observers have approached the subject; for in this way it seemed that more light might be thrown upon the phenomena than would be obtained by the detailed consideration of one or two of the hypotheses. It must be borne in mind that a complete theory of colloids would have to account for at least the following: (1) the difference between crystalloids and colloids; (2) the difference between suspensoids and emulsoids; (3) the phenomena of coagulation; (4) the surface action of colloids which is manifested in adsorption; (5) the electrical properties of colloidal materials. There are, of

Digitized by Google

course, other matters which also demand explanation; but unless these five are satisfactorily dealt with there can be no full treatment of the problem. As will be seen in the following sections, there is as yet no hypothesis which covers the ground in its entirety.

2. *The Crystalloid Hypothesis.*

In the course of his earliest work upon colloids, Graham[1] made the following suggestion: "The inquiry suggests itself whether the colloidal molecule may not be constituted by the grouping together of a number of smaller crystalloid molecules, and whether the basis of colloidality may not really be this composite character of the molecule".

Graham does not seem to have pushed the matter beyond a mere surmise; and it is doubtful if he regarded his suggestion as more than a guess: but this crystalloid hypothesis, though vague, is of some interest when considered in relation to the knowledge which Graham possessed at the time he put it forward. If the case of silicic acid be taken as an example, the implications of the crystalloid hypothesis can most easily be seen. In the highest degree of subdivision imaginable, silicic acid must on this hypothesis be supposed to exist in the form of extremely minute crystals. In this form, it is capable of yielding a homogeneous sol; but in this sol the tiny crystals become collected together into aggregates which lend to the liquid its colloidal properties. When a higher degree of aggregation is attained, the material takes the form of a gel.

This suggestion of Graham has been extended by von Weimarn[2] to include all states of matter. According to von Weimarn, the crystalline condition is common to all matter, whether solid, liquid or gaseous. As far as the gaseous state is concerned, it is unnecessary to consider the hypothesis further, but one or two points may be mentioned in connection with the liquid condition.

By carrying out a series of precipitations over wide ranges of concentration, von Weimarn observed that certain concentrations favoured the formation of crystalline precipitates whilst greater or less concentrations had the effect of producing

[1] Graham, *Phil. Trans.*, 1861, **151**, 183.
[2] von Weimarn, *Kolloid Zeitsch.*, 1907, **2**, 81.

Digitized by Google

materials which inclined more and more to the amorphous character, even when examined under the microscope. With increasing dilution of the solution, the magnitude of the crystals diminished; and von Weimarn assumed that in the extremes of dilution the precipitated particles were still crystalline, though so tiny that their crystalline character could not be recognised even by means of the microscope.

Thus, according to von Weimarn, all matter, when in its finest state of division, assumes the crystalline character; and the particles of a colloidal material are built up by the aggregation of these extremely minute crystalline bodies.

In this connection, the occurrence of liquid crystals[1] is of some interest. When para-azoxy-anisol is heated, it melts sharply at 116° C. forming a turbid liquid which, on further heating, suddenly becomes clear at 134° C. When the clear liquid is cooled down again, the phenomena take place in the reverse order: the clear liquid becomes turbid and finally solidifies. Examination of the turbid material shows that it has a dual set of properties. It behaves like a true liquid, flowing under the action of gravity and assuming a spherical form when immersed in another liquid of the same density with which it does not mix; but in addition it exhibits the property of double refraction which is possessed by certain crystals. This behaviour is not peculiar to a single compound, for quite a large group of substances exhibit the phenomena almost equally well.

These facts suggest the question whether the turbid liquid is homogeneous or is composed of a solid and a liquid phasis. In other words, is it a homogeneous liquid or an emulsion? An observation of Mauguin throws some light upon the point. When the illumination used in the microscope is very intense, it is found that even when the polariser and analyser are brought into the position of extinction the light does not vanish completely. Instead, there is an incessant scintillation in the field which recalls the swarming of an ant-heap.[2] This appearance certainly suggests an emulsion and Mauguin regards the phenomenon as akin to the Brownian movement. In any case, the presence of crystalline properties in these materials certainly

[1] Lehmann, *Flüssige Krystalle*; Vorländer, *Krystallinisch-flüssige Substanzen.*

[2] Perrin, *Les Atomes*, 1913, p. 203; *Atoms*, 1916, p. 143.

Digitized by Google

points to the existence of some crystalloid character in extremely minute particles of matter; and to this extent it may be regarded as supporting von Weimarn's hypothesis.

It must be borne in mind, however, that even if the crystalloid hypothesis of colloidal solutions be accepted, it leaves untouched the whole of the electrical properties of colloids; so that it cannot be regarded as anything more than a first attempt to account for the phenomena.

3. *The Solution Hypothesis.*

From time to time the idea has been put forward, either explicitly or implicitly, that colloid sols might be regarded as true solutions in which the solute consisted of very large molecules. The fact that sols exhibited the phenomena of osmotic pressure was regarded by some as a proof that they resembled ordinary solutions, even though the observed pressures were very slight.

This solution hypothesis, however, can hardly be regarded as sound at the present day. In the first place, the phenomena of osmotic pressure have been shown by Perrin to be manifest in emulsions where the particles are so large as to be visible to the microscope; and it can hardly be supposed that the spheres of gamboge which he observed were truly "molecular" in character. Secondly, a true solution is supposed to be homogeneous; whilst the ultramicroscope reveals the fact that the particles in either an emulsoid or a suspensoid are by no means uniform; and even the naked eye is sufficient to detect the inhomogeneity of a centrifuged gold sol, owing to the range of tints which it displays at different heights in the tube. Finally, the solution hypothesis furnishes no explanation of coagulation or the electrical properties of colloids.

It may therefore safely be concluded that no mere solution hypothesis can account for the phenomena; and the idea is mentioned here only for the sake of completeness.

4. *The Partition Hypothesis.*

In order to make clear the partition hypothesis of colloids, it will be best to recall a familiar example of two partially miscible materials: phenol and water. When phenol is added

Digitized by Google

to water, a homogeneous liquid is formed (solution of phenol in water) until the concentration of the phenol reaches about 8 per cent., at which point saturation is attained at ordinary temperatures. Further addition of phenol results in the formation of two layers, one of which consists of a solution of phenol in water whilst the other is a solution of water in phenol. On raising the temperature of the liquid, the solubility of phenol in water and the solubility of water in phenol are both increased; and, finally, the two layers become identical in composition and the liquid becomes homogeneous at about 68° C.

Now apply the same ideas to the case of gelatine and water. When the gelatine is first added to an excess of water, solution occurs and a homogeneous liquid is produced. The addition of more gelatine brings the solution to the point of saturation and the further rise in gelatine concentration leads to the formation of two layers containing different proportions of water. By increasing the temperature, it is possible to bring the whole of the gelatine into solution, just as the phenol-water system could be made homogeneous.

Van Bemmelen drew attention to the fact that gels are materials with a structure [1] the semi-solid membranes of which contain some of the sol-liquid. In other words, the system may be regarded, according to him, as built up from two different materials: a solution of the sol in the gel and a solution of the gel in the sol. Naturally, as in the case of phenol and water, this system can be influenced by changes of temperature or the addition of salts to the liquid. As van Bemmelen showed, the removal of water from colloidal hydroxides is a continuous process and does not occur in definite stages as is the case when water of crystallisation is removed step by step from a polyhydrated salt.

On somewhat similar lines, Spiro and Hofmeister [2] have attempted to account for the precipitation of colloids. Imagine that when alcohol is added to a hydrosol the colloid is precipitated. The system is then a two-phase one containing the three components: colloid, alcohol and water. Since the alcohol and water are completely miscible, it is evident

[1] Bütschli, *Microscopic Foams and Protoplasm*, 1894.

[2] Hofmeister, *Arch. exp. Path. Pharm.*, 1890, **27**, 395; 1891, **28**, 210; Spiro, *Beiträge chem. Physiol. Path.*, 1903, **4**, 320.

Digitized by Google

that the liquid will contain alcohol and water in definite proportions; but the relation of colloid to alcohol in the precipitated portion is not the same as it is in the unprecipitated part of the colloid. The precipitated phase is obviously weaker in solvent than the original solution was. This has actually been proved to be the case in gelatine solutions when a series of precipitations was carried out with salt solutions of gradually increasing concentration. Thus the process of precipitation is really one in which the colloid is deprived of solvent.

This hypothesis of coagulation is, however, very incomplete, as it fails to take into account many important factors in the problem, such as surface tension, viscosity and electrical character.

5. *The Negative Surface Tension Hypothesis.*

Donnan[1] suggested that under certain conditions it is possible for a substance to exhibit a negative surface tension; and he has applied this idea to the case of colloids in the following manner: When a mass of material is placed in a liquid, two forces are at work: a cohesive force acting between the molecules of the liquid and those of the solid; and an adhesive force acting between molecule and molecule of the solid. If the force of cohesion is greater than that of adhesion, particles will be torn off the surface of the solid, which will thus diminish in volume; but as the volume of the solid diminishes, the liquid layer about it becomes thinner and thus the cohesive force is decreased. Obviously at some stage or other, the cohesive and adhesive forces will come into a balance; and after this there will be no change in the size of the solid mass.

There is, according to this hypothesis, a critical size of grain for each colloid, the magnitude being determined by the relationship between the cohesive and adhesive forces in the system. Particles smaller than this critical grain will tend to increase in size by a process of aggregation; while particles of larger size will be reduced by the tearing off of fragments under the action of the cohesive forces.

[1] Donnan, *Phil. Mag.*, 1901, **17**, 647; *Zeitsch. physikal. Chem.*, 1901, **37**, 713; 1903, **46**, 197.

Digitized by Google

While there is much of interest in this speculation, it must be pointed out that it certainly cannot be applicable to all colloidal solutions, for in the case of gold sols, for example, it is experimentally proved that particles of widely different dimensions exist in the same solution; and this seems to hold good in the case of many emulsoids. The Donnan hypothesis, like many of our mathematical solutions, must be regarded merely as a first approximation to the truth. It leaves out of account altogether the electrical properties of colloids, although these furnish several of the most characteristic features differentiating colloids from crystalloids.

6. *Electrical Hypotheses.*

From what has been said in previous chapters, it is evident that electrical charges play a very important part in the behaviour of certain colloids; and it is therefore natural to look to the action of these electrical charges as a cause of processes such as coagulation and hence to endeavour to explain the stability of colloidal solutions upon some electrical basis.

According to Hardy,[1] the particles of a colloid may be charged with, say, positive electricity, whilst the liquid in which they float carries a charge of the opposite sign. Under these circumstances, stability of the colloid is, under certain conditions, ensured; for there can be no aggregation of the particles into larger masses owing to the repulsive effect of the charges upon each other. If the particles be discharged by the addition of ions of the opposite sign, then coagulation ensues through gravitational attraction.

Similar views were put forward by Bredig,[2] but he pointed out that the removal of the charge from a colloid particle would leave the surface tension of the particle free to produce a centripetal movement of the particles, thus causing coagulation.

These ideas have been criticised by Billitzer[3] on the

[1] Hardy, *Zeitsch. physikal. Chem.*, 1900, **33**, 385.

[2] Bredig, *Anorganische Fermente*, p. 15.

[3] Billitzer, *Zeitsch. Elektrochem.*, 1902, **8**, 638; *Wien. Ber.*, 1902, **111**, 1393; 1903, **112**, 95; 1904, **113**, 1159; *Zeitsch. physikal. Chem.*, 1903, **45**, 307; 1904, **51**, 129.

Digitized by Google

ground that they fail to account for the precipitation of emulsoids and suspensoids by the addition of alcohol, which can have no electrical action. Billitzer's own hypothesis with regard to the action of ions upon colloids is that they form centres of aggregation around which the colloidal particles agglomerate, just as particles of water agglomerate around ions in air within the "dust-counter" of C. T. R. Wilson.

7. *Conclusion.*

The foregoing hypotheses are sufficient to show some of the ways in which attempts have been made to solve the colloid problem. Many other views might have been added to those given above; but the object in this chapter has been merely to illustrate the matter, not to give a full account of it; and the selection has been made with this aim in view.

In the case of so ill-defined a phenomenon as the colloidal state, it can hardly be expected that a single hypothesis will suffice to account for all the known facts; and it seems probable that the truth includes more than one of the factors which have been dealt with singly in the foregoing sections. The difference between suspensoids and emulsoids alone is sufficient to discount the possibility of covering the whole ground by a single hypothesis; and the demarcation between reversible and irreversible coagulation seems to point to the entry of chemical factors into certain regions of the subject.

Digitized by Google

CHAPTER XV.

CATALYSIS.

1. *Some Criteria of Catalytic Action.*

AMONG the most confusing names in the chemical field, "catalysis" must be awarded a high place. The confusion which has arisen is to a large extent due to the fact that under the same heading a large number of actions have been included which often show little resemblance among themselves and which are due to entirely different causes; and, owing to this, it has become difficult to define exactly what is meant by catalytic action.

For example, take three well-known processes: the combination of hydrogen and chloride under the action of light; the reactions between sulphur dioxide, oxygen and the oxides of nitrogen in the sulphuric acid chamber process; and in the contact process the combination between sulphur dioxide and oxygen in presence of spongy platinum. In the first case the reaction is stimulated by the application of radiant energy; in the chamber process, an intermediate compound is formed; whilst in the case of the contact process, surface action is believed to be the cause of the acceleration of the reaction. Yet all three are grouped under the head of catalytic action. This grouping appears to be on the same plane as one which would classify together a rowing-boat, a wheel-barrow and an aeroplane, on the ground that all three are contrivances for transporting goods from one place to another.

From this it will be seen that any attempt to systematise the field of "catalytic action" is almost certain to be a failure in some direction or other; and this caution must be borne in mind throughout the present chapter. All that can be done is to deal with the subject in its broadest outlines; and even in them there is sure to be a certain inconsistency. The

Digitized by Google

following criteria[1] have been drawn up to cover the case in which the catalyst is an actual material body; and the case of radiation effects has been left out of account.*

1. *At the beginning and the end of the reaction, the catalyst has the same chemical composition, though not necessarily the same physical state.*—The first part of this criterion seems to be definitely established in the catalytic action of finely divided metals, as well as in other cases of a more complex type. With regard to the second provision, a single example will suffice. The action of manganese dioxide in promoting the liberation of oxygen from potassium chlorate is well known. Now, when crystalline manganese dioxide is introduced as a catalyst, it is found that at the end of the process the dioxide has lost its crystalline form and has become converted into the amorphous variety.[2] Thus apparently in the course of its catalytic action it has undergone an alteration in physical condition.

2. *A small quantity of catalyst is sufficient to act upon an indefinitely large quantity of the reacting substance.*—One of the most striking examples of this is mentioned by Titoff,[3] who found that the rate of oxidation of sodium sulphite in aqueous solution was perceptibly accelerated by the presence of copper sulphate having a strength of only 0·0000000000001 normal. Again, 0·0004 gramme of colloidal platinum has been found capable of bringing about combination in a mixture of ten litres of oxygen and hydrogen.[4]

3. *A catalytic agent is incapable of starting a reaction; its action is confined to modifying the velocity of an existing reaction.*—A considerable amount of controversy has raged round this criterion; but the matter seems to be one of academic interest, since it is incapable of decisive proof. In order to prove it, it would be necessary to establish that, say,

[1] See Mellor, *Chemical Statics and Dynamics*, 1904, pp. 246 ff., for further notes on these criteria.

[2] Sodeau, *Trans.*, 1900, **77**, 137, 717; 1901, **79**, 247, 939; 1902, **81**, 1066.

[3] Titoff, *Zeitsch. physikal. Chem.*, 1903, **45**, 641.

[4] Ernst, *ibid.*, 1901, **37**, 448.

* It seems doubtful if the action of radiant energy can properly be quoted as an example of catalysis since the so-called "catalyst" in this case is certainly altered during the action owing to the absorptive power of the substances on which it acts.

Digitized by Google

oxygen and hydrogen, when free from any catalyst, did not combine together at all; and this would involve observations extending over a more prolonged period than is convenient; while the further difficulty arises that the sides of the containing vessel might act as catalysts so that a "blank" control experiment would be impossible. The point seems of little importance at the best, since certainty upon it can never be attained.

4. *A catalyst cannot affect the final state of equilibrium of the system into which it is introduced.*—This criterion must hold good unless the laws of thermodynamics are to be rejected. Suppose that an isolated system comes into a state of equilibrium (I.) and that in presence of a catalyst it passes into a fresh state of equilibrium (II.). On removing the catalyst, it will return to equilibrium (I.), thus occasioning a change of energy. Therefore, by alternately introducing and removing the catalyst, energy could be obtained from the system, which is impossible unless perpetual motion be granted.

5. *The velocities of two inverse reactions are equally affected by the catalyst.*—This follows naturally from the statement above; for if the velocities of the two parts of a reversible reaction were differently affected by the catalyst, then the state of equilibrium of the system would be altered by inserting and removing the catalyst. There are, however, cases in which there is an apparent deviation from the rule. For example, when a solution of hydroxylamine is heated, the products are ammonia, nitrogen, water and traces of nitrous oxide; but when platinum black is present, the proportion of nitrous oxide is considerably increased.[1] In this case, however, the matter is explained by the fact that there are two possible reactions:—

$$3NH_2OH = NH_3 + N_2 + 3H_2O$$
$$4NH_2OH = 2NH_3 + N_2O + 3H_2O$$

The presence of the catalyst evidently accelerates the second type of reaction more than the first, so that more nitrous oxide makes its appearance in the end-products.

6. *The state of equilibrium is independent of the quantity*

[1] Tanatar, *Zeitsch. physikal. Chem.*, 1902, **40**, 475; **41**, 37; Berthelot, *Ann. chim. phys.*, 1877, **10**, 433; 1890, **21**, 384.

Digitized by Google

and the nature of the catalyst.—This statement is apparently accurate. The first clause of it follows from what has already been said with regard to the laws of thermodynamics; for if the quantity of the catalyst influenced the position of equilibrium, then energy could be derived from the system by increasing and decreasing the amount of catalyst present. With regard to the second clause, it has been shown that the same equilibrium state is attained between acetaldehyde and paraldehyde, whether sulphur dioxide, zinc sulphate, hydrogen chloride, oxalic acid or phosphoric acid be employed as a catalyst.[1]

2. *Positive and Negative Catalysis.*

The term *positive catalysis* is used to describe the action of a catalyst which increases the velocity of a reaction. For example, the normal rate of oxidation of methyl alcohol in air is very slow; but in presence of spongy platinum the vapour of methyl alcohol is oxidised so rapidly that the heat evolved by the reaction is sufficient to raise the temperature of the platinum considerably, even at times to a red heat.

Curiously enough, the action of a catalyst may in some cases be increased by the presence of other substances, so that it is possible to suppose that the catalytic process itself may be catalysed. For example, in the oxidation of aniline or naphthalene by means of sulphuric acid, it is found that a mixture of mercuric and copper sulphates exerts a catalytic influence greater than the sum of their separate effects.[2] Again, when reduced iron is employed as a catalyst, it is found that its activity is considerably increased by the presence in it of traces of molybdenum, tungsten or uranium. These are termed *promoters.*

The term *negative catalysis* has been employed in two senses. In the first of these, it expresses the process inverse to positive catalysis—*i.e.*, a case in which the presence of the catalyst inhibits the normal course of a reaction. A well-known example of this is to be found in the preservation of hydrogen peroxide solutions in presence of sulphuric acid,

[1] Turbaba, *Zeitsch. physikal. Chem.*, 1901, **38**, 505; *Zeitsch. Elektrochem.*, 1902, **8**, 70.

[2] Bredig and Brown, *Zeitsch. physikal. Chem.*, 1908, **46**, 502.

Digitized by Google

which seems to reduce the instability of the peroxide. Another instance is to be found in the protective action of substances like mannite, benzaldehyde or benzyl alcohol in the oxidation of sodium sulphite by air.[1]

The term has also been applied to cases in which the action of one catalyst is paralysed by the presence of traces of another material. For example, if colloidal platinum be employed as a catalyst, it is found that its catalytic power is markedly diminished in presence of hydrocyanic acid, halogens, carbon disulphide, phenol and many other substances.[2] Here, apparently, the process is the inverse of that which takes place in the action of a promoter.[3]

In connection with these "secondary catalytic phenomena" mention may be made of what is known as *auto-catalysis* and *auto-retardation*. It is sometimes found that when a trace of a catalyst is added to two reagents these begin to interact slowly but thereafter the reaction proceeds with ever-increasing rapidity until the equilibrium point is reached. This cannot be accounted for by the ordinary ideas of catalysis, since a given quantity of catalyst can be imagined only as dealing with equal quantities of the reagents in equal times; so that the reaction should proceed at a uniform rate in accordance with the mass-action law.

A concrete example will serve to make the point clear. When methyl acetate is hydrolysed by means of sodium hydroxide, the reaction follows the course—

$$CH_3.COOCH_3 + NaOH = CH_3.COONa + CH_3.OH$$

This is an ordinary bimolecular reaction; and if at the start there be present a gramme-molecules of sodium hydroxide and b gramme-molecules of methyl acetate, the velocity of the reaction can be expressed by the equation—

$$\frac{dx}{dt} = k(a - x)(b - x)$$

This is the normal state of things in a bimolecular reaction; and it should be noticed that in this case the hydrolysing

[1] Bigelow, *Zeitsch. physikal. Chem.*, 1898, 26, 493; 27, 585.

[2] Ernst, *ibid.*, 1901, 37, 448; see also Bredig, *Anorganische Fermente.*

[3] A full account of the phenomena is to be found in Bancroft's paper, *J. Physical Chem.*, 1917, 21, 767.

Digitized by Google

agent—the sodium hydroxide—disappears regularly during the reaction, as it becomes converted into sodium acetate.

On the other hand, when methyl acetate and water are brought into contact, the hydrolysis of the ester can be catalysed by the addition of a trace of acetic acid to the mixture. The reaction takes the following course:—

$$CH_3.COOCH_3 + H_2O = CH_3.COOH + CH_3.OH$$

Now in this case, for every molecule of ester hydrolysed, one molecule of acetic acid is liberated; and this acid at once begins to play the part of a catalyst in the reaction. Thus as the reaction progresses there is present an ever-increasing quantity of catalyst, and the reaction velocity naturally increases from instant to instant.

Suppose that there are a gramme-molecules of acetic acid and b gramme-molecules of methyl acetate present at the start. The initial velocity of the hydrolysis will be representable by—

$$\frac{dx_1}{dt} = k_1 a(b - x)$$

since the rate of hydrolysis is proportional to the quantity of catalyst present. Now assume that at the time t there are x gramme-molecules of acetic acid liberated by the reaction. These x gramme-molecules of acid also act catalytically, increasing the velocity, so that their action can be expressed thus—

$$\frac{dx_2}{dt} = k_1 x(b - x)$$

The true velocity of the reaction will therefore be representable as the sum of these two separate velocities, *i.e.*, as—

$$\frac{dx}{dt} = \frac{dx_1}{dt} + \frac{dx_2}{dt} = k_1(a + x)(b - x)$$

which is obviously different from that of a normally catalysed reaction.

Auto-retardation depends upon a process similar to that of auto-catalysis. A reaction may give rise to some substance which has a retarding influence upon the reaction; and in that case there will be a slowing down of the reaction velocity as more and more of the inhibitory compound is thrown into the system.

Digitized by Google

3. *Selective Catalysis.*

In the case of the decompositions of hydroxylamine, it has already been pointed out that when two reactions proceed side by side a catalyst may accelerate one of them to a greater extent than the other. That selective action of the catalyst furnishes one of the most interesting subjects in this field of chemistry; and its extension into the province of biochemistry links it with some of the most fundamental properties of living tissue. One or two examples of selective action may be given here in order to bring out the peculiarities of the processes involved.

When benzaldehyde and hydrocyanic acid are allowed to react together in presence of hydrochloric acid as a catalyst, the nitrile of mandelic acid is formed:—

$$\underset{\text{Benzaldehyde.}}{C_6H_5 . CH : O} + H . CN = \underset{\text{Mandelonitrile.}}{C_6H_5 . \overset{*}{C}H(OH) . CN}$$

By hydrolysis, the mandelonitrile can be converted into the ammonium salt of mandelic acid:—

$$C_6H_5 . \overset{*}{C}H(OH) . CN + 2H_2O = C_6H_5 . \overset{*}{C}H(OH) . COONH_4$$

It will be noticed that in the formulæ of the nitrile and of the ammonium salt the carbon atom marked with an asterisk is asymmetric, being attached to four different groups; so that the two compounds are capable of appearing in optically active forms. When hydrochloric acid is used as a catalyst in the formation of the nitrile, it is found that the right and left-handed forms are produced in exactly equivalent quantities, so that no optical activity is shown by the product owing to the *dextro*-rotation of the one portion exactly counterbalancing the *lævo*-rotation of the other portion.

When, however, benzaldehyde and hydrocyanic acid are allowed to unite in presence of quinine as a catalyst, the end-product of the reaction contains a preponderance of the *lævo*-rotatory form of mandelonitrile. If for quinine there be substituted the stereoisomeric alkaloid quinidine, the proportions are inverted; and the reaction product contains more *lævo*- than *dextro*-mandelonitrile. From these results[1] it is evident

[1] Bredig and Fiske, *Biochem. Zeitsch.*, 1912, **46**, 7; Fajans, *Zeitsch. physikal. Chem.*, 1910, **73**, 25,

Digitized by Google

that a "symmetrical" catalyst such as hydrochloric acid produces the two optically antipodic forms of mandelonitrile in equal quantities; whereas an "asymmetrical" catalyst favours the production of one of the possible antipodes at the expense of the other; and the nature of the favoured form depends upon the stereochemical nature of the asymmetrical catalyst employed.

The results in these cases can hardly be attributed to the influence of the alkaloids merely as part of the solvent used in the reaction, for it has been shown that no such asymmetric process occurs when an asymmetric carbon atom is brought into existence in a molecule dissolved in an optically active solvent.[1] It must therefore be inferred that in this case the alkaloidal catalyst actually enters into chemical combination with the aldehyde and acid during the synthetical process and that this intimate union permits its stereochemical character to influence the nature of the end-product.

The same selective action is observed when the enzyme emulsin is substituted for hydrochloric acid in the mandelonitrile condensation. In presence of this enzyme, the main reaction product is the *dextro*-rotatory form of the nitrile.[2]

In the group of the sugars, analogous influences are found to be at work.[3] The following five stereochemical formulæ will suffice to illustrate the point under consideration:—

CHO	CHO	CHO	CHO	CHO
H . OH	HO . H	CO	H . OH	HO . H
HO . H	HO . H	HO . H	HO . H	HO . H
H . OH	H . OH	H . OH	HO . H	HO . H
H . OH	H . OH	H . OH	H . OH	H . OH
CH_2OH	CH_2OH	CH_2OH	CH_2OH	CH_2OH
Glucose.	Mannose.	Fructose.	Galactose.	Talose.

Inspection of the heavily printed portions of the five formulæ will show that the configurations of the three left-hand ones resemble each other closely, despite the fact that

[1] Boyd, *Dissertation*, Heidelberg, 1896; Kipping, *Proc.*, 1900, **16**, 226; Wedekind and Wedekind, *Ber.*, 1908, **41**, 456; Bredig and Balcom, *Zeitsch. physikal. Chem.*, 1899, **32**, 2130.

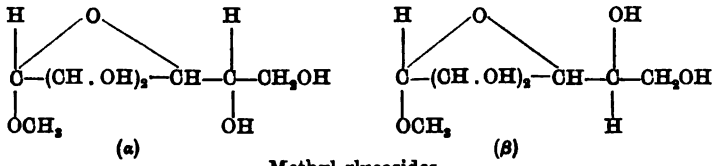
[2] Rosenthaler, *Biochem. Zeitsch.*, 1909, **14**, 238; Auld, *Trans.*, 1909, **95**, 927; compare Feist, *Arch. Pharm.*, 1909, **247**, 226.

[3] Fischer, *Zeitsch. physikal. Chem.*, 1898, **26**, 60; compare Ehrlich, *Biochem. Zeitsch.*, 1906, **1**, 8.

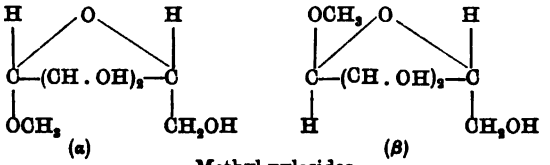
Digitized by Google

fructose has a carbonyl radicle instead of the —CH(OH)— group in its structure; but the space formulæ of galactose and talose diverge considerably from the model of the other three. Now, when ferments are allowed to act upon these sugars, it is found that glucose, mannose and fructose are readily fermented; galactose is less readily attacked; whilst talose is almost unaffected by the ferment which destroys the others. From this it appears evident that the catalytic action of the ferment is markedly influenced by the space formula of the compound upon which it acts.

Again the same influence is found to be at work in the case of the glucosides:—



Methyl-glucosides.



Methyl-xylosides.

In the formulæ of the methyl-glucosides it will be noticed that the difference between the two compounds lies in the different arrangement of the hydrogen and hydroxyl at the right-hand end of the chain. In the methyl-xyloside formulæ the space difference is symbolised by the change in the position of the hydrogen and methoxy radicles. This difference may seem very slight, but it exerts a considerable influence upon the catalytic effects of emulsin and yeast upon the compounds. The α-methyl glucoside is attacked by yeast, the β-form by emulsin; but neither emulsin nor yeast is able to attack the methyl-xylosides, in the formulæ of which the penultimate —CH . OH— group of the glucosides is missing.

These results and others led Fischer to propound his simile of a lock and key in connection with enzyme action. In order that the action of the enzyme may be as complete as possible,

Digitized by Google

the enzyme's configuration must fit that of the sugar as closely as possible. When only certain parts of the enzyme configuration fit in with the sugar, then the action between the two compounds is incomplete, just as an ill-suited key may turn certain wards in a lock without succeeding in unlocking it entirely.

4. *The Solvent Medium as a Catalyst.*

Some authors have included solvents in the class of catalytic agents; and it may be well to examine more closely the limitations which must be placed upon any such conception.

In the first place, if a catalyst be defined as a substance which can be recovered unchanged at the end of the reaction, it is clear that by this definition we exclude from the catalyst class all solvents which take part in a reaction. For example, when acetic acid is dissolved in alcohol preparatory to the formation of an ester, it is evident that part of the alcohol will take part in the esterification reaction; and that, therefore, alcohol cannot be regarded as a real catalytic agent, even if it exerted any catalytic influence.

When the solvent plays no part as an actual reagent, it is possible to regard it as a catalytic agent; but the problem is complicated by the fact that we know very little about the factors which govern solubility. It has been pointed out on previous pages that a catalyst may vary in its action according to the nature of the material upon which it acts and also that it may stimulate one reaction while leaving a parallel reaction almost unaffected. Now, in the case of solvents, a rough parallelism to this latter action may be detected. For example, in aqueous solution the interaction of mercuric chloride and potassium iodide results in the precipitation of mercuric iodide; whereas the same reagents in acetone solution give rise to a precipitate of potassium chloride. Here, evidently, we might speak of a "directive influence" of the solvent, which leads to the favouring of one reaction rather than another; but in view of our ignorance of solution phenomena, it is hardly safe to do more than point to the apparent parallelism between the cases of catalyst and solvent.

Instead of considering solvents in general, it will suffice for the present purpose to confine attention to the case of water.

Digitized by Google

When two different salts are dissolved in water, the rate of reaction between them is greatly increased owing to the formation of ions; yet the water can in most cases be recovered intact after the reaction is terminated. Further, a very small quantity of water is sufficient to convert an unlimited quantity of the initial materials into the end-products in the case where the latter are insoluble.* In its capacity as an ionising medium, then, water may reasonably be regarded as a catalytic agent.

In some reactions it is found that the presence of liquid water is necessary. For example, at 100° C. oxygen and sulphur dioxide do not combine in presence of water vapour, though when a particle of liquid water is introduced into the system, oxidation takes place at once.[1] Even in the state of vapour, however, water can exert a catalytic influence, as was first pointed out by Dixon[2] and later confirmed by the work of Baker.[3] Water is found to act both as a positive and as a negative catalyst. In the combination between carbon monoxide and oxygen, it plays the part of an oxygen carrier and assists the combustion; whereas in the decomposition of diazoacetic ester[4] the presence of water has an inhibitory effect upon the reaction. In view of the fact that hydrogen and hydroxyl ions are known to exert catalytic effects, it seems possible that some of the catalytic phenomena observed in the case of water may be due to the presence of these ions.

5. *Some Theories of Catalytic Action.*

Catalytic processes may be grouped under the following heads: (1) heterogeneous catalysis; (2) homogeneous catalysis. In *heterogeneous catalysis*, the catalyst and the reacting substances are in different states of aggregation, as, for example, when hydrogen and the vapour of an unsaturated hydrocarbon are combined in presence of finely divided metals in the Sabatier and Senderens method or when the decomposition of a solution of hydrogen peroxide is catalysed by particles of

[1] Dixon, *Journal of Gas Lighting*, 1881, **37**, 704.

[2] Dixon, *Brit. Assoc. Rep.*, 1880, 593; see also Mrs. Fulhame, *An Essay on Combustion*, 1794, for a foreshadowing of this.

[3] Baker, *Trans.*, 1894, **65**, 611.

[4] Bredig and Fränkel, *Ber.*, 1908, **39**, 1756.

* Compare the case of the tartrates and racemate of rubidium on p. 50.

Digitized by Google

colloidal platinum. In cases of *homogeneous catalysis*, the catalyst is in the same physical condition as the reagents, as in the catalytic action of nitric oxide in the Chamber Process, where all the materials are gaseous, or in the case of the inversion of cane-sugar by the aid of acid, where the whole system is a solution.

The theories of catalytic action which have been put forward from time to time are very numerous; and here it will be possible only to give an outline of the more important ones.[1]

Theories founded on Adsorption or Surface Action.—In the course of his investigations upon the power of metals to induce the combination of gases[2] Faraday was led to the conclusion that since gases may suffer very great changes in the relative distances of their particles by external agencies, the approximation of those particles may be very great when the gases are attracted to and held by the surface of, say, platinum;[3] and it was to this state of affairs that he attributed the readiness to react which is shown by certain gases when placed in presence of metals. To express the matter in modern language, Faraday believed that the two reacting gases were adsorbed by the platinum, and that being thus brought into intimate contact with each other, they proceeded to interact.

Clearly this hypothesis implies that the area of the exposed surface of the metal will be one of the governing factors in the problem, since the greater the surface, the larger is the quantity of adsorbed material which can find a place upon it. Actually, of course, it is found that the more finely divided the metal is, the greater is its catalytic power; so that the adsorption theory is in agreement with the facts. Again, the degree of adsorption varies from gas to gas for the same solid adsorbing medium;[4] and it is possible on this ground to explain the "poisoning" effect which is exerted by some gases upon finely divided platinum. If the "poison" is strongly adsorbed by the metallic surface whilst the reacting gases are weakly adsorbed, it is evident that the main part of the adsorbing surface will be occupied by molecules of the "poison" and consequently there

[1] For further information see Mellor, *Chemical Statics and Dynamics*, and Rideal, *Catalysis in Theory and Practice*.

[2] Faraday, *Experimental Researches*, Sixth Series, Vol. I., p. 165.

[3] Faraday, *loc. cit.*, paragraph 361.

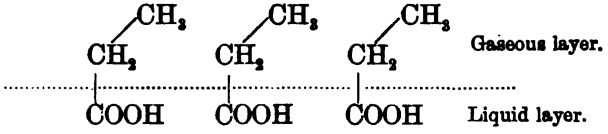
[4] See Bancroft, *J. Physical Chem.*, 1917, 21, No. 8.

Digitized by Google

will be less of it free to adsorb the reagents which it is desired to bring into combination.

Another view of surface action is due to J. J. Thomson.[1] According to him, adsorption is accompanied by a change in the physical state of the adsorbed material. In the case of a solution spread out in thin films, the influence of capillarity is very great and in certain cases it may become so great that it may alter the state of equilibrium in a system. Surface tension depends upon the nature and the concentration of the system which exhibits it; so that if the system is undergoing chemical change, the surface tension must be altering concurrently. Now Thomson has shown that if the surface tension increases as chemical action proceeds, the influence of capillarity will be exerted against the chemical action; whereas if the chemical action is tending to produce a lowering of the surface tension, the capillarity of the system will favour the reaction.

It has been suggested by Langmuir[2] that, in addition to the mechanism of ordinary adsorption, an orientation of molecules occurs in certain cases. For example, when a thin film of a fatty acid is allowed to float upon water, Langmuir supposes that the carboxyl groups congregate in the aqueous layer whilst the hydrocarbon radicles spread upward into the gaseous region above:—



The good results obtained in the hydrolysis of fats by means of Twitchell's reagent lend a certain amount of support to Langmuir's views. The Twitchell reagent is prepared by the action of concentrated sulphuric acid upon a mixture of oleic acid and some aromatic hydrocarbon such as benzene or naphthalene; by which process a sulphonic acid is produced. This acid fulfils all the requirements of the process of hydrolysis: it is a strong acid and an active catalyst; owing to

[1] J. J. Thomson, *Application of Dynamics to Physics and Chemistry*, 1888, pp. 206, 236.

[2] Langmuir, *J. Amer. Chem. Soc.*, 1916, **38**, 2221; 1917, **39**, 1848; 1918, **40**, 1361.

Digitized by Google

the presence of the acidic group it is soluble in water; and since it contains a hydrocarbon chain it dissolves in the fat upon which it is to act. The oleic chain helps the material to produce a soapy solution which promotes the intimate commingling of the various substances present. On Langmuir's hypothesis, any molecules lying on the border-line between fat and watery layers would have the hydrocarbon portion dissolved in the fatty layer and the acidic part dissolved in the aqueous layer.

The Intermediate Compound Theory of Catalysis.—This conception of the catalytic process involves the assumption that the catalyst acts as a "carrier" in the transference of certain atoms from one compound to another. The rationale of the process may be illustrated by the preparation of chlorine from hydrochloric acid by oxidation in presence of the catalyst cupric chloride:—

(1) $4CuCl_2 = 2Cu_2Cl_2 + 2Cl_2$

(2) $2Cu_2Cl_2 + 4HCl + O_2 = 4CuCl_2 + 2H_2O$

It is obvious from the above equations that the cupric chloride decomposes, yielding chlorine; and that the cuprous chloride thus formed then combines with more chlorine in the second stage of the reaction, regenerating cupric chloride. Thus a small quantity of cupric chloride will serve to convert an unlimited amount of hydrochloric acid and oxygen into chlorine and water.

In some cases it is impossible to isolate the intermediate compounds which are assumed to be produced during the reactions. For example, when copper salts are employed as catalysts in the oxidation of aniline to aniline black, it has not been possible to establish the oscillation of the copper between the cuprous and cupric states, though this change is supposed to lie at the root of the process.

Even in such cases, however, it is sometimes possible to observe suggestive phenomena. For example, when copper gauze is employed as a catalyst in the conversion of methyl alcohol into formaldehyde at low temperatures, it is found that the colour of the gauze surface undergoes periodic changes.*

* This can be seen by heating a small roll of copper gauze and dropping it while hot into a test-tube containing a few drops of methyl alcohol. Variations in the colour of the gauze are easily seen.

Digitized by Google

From these colour-changes it is inferred that an alternate oxidation and reduction of the copper is taking place.

Even in the case of an inert metal like platinum, surface changes occur which lend support to the intermediate compound theory. Platinum gauze which has been used as a catalyst in the oxidation of ammonia is found, after a time, to have changed its structure; the clean surface of the wires becomes covered with a spongy-looking deposit of the metal. It has been suggested that this change in surface structure is due to a process of alternate oxidation and reduction of the platinum. If an oxide be formed, it is hardly likely to be PtO, since this appears to have very poor catalytic qualities; and the suggestion has been made that PtO_2 may be the intermediate product in this instance.

In some cases, instead of an oxide, the formation of an intermediate hydride of a metal is assumed to be a step in the process. For example, in the Sabatier and Senderens method of reduction in presence of finely divided metals, it is suggested that the hydrogen attacks the metal, forming a hydride which then yields up its hydrogen to the material under treatment.[1]

Ionic Theories of Catalytic Action.—When either acid or alkali is added to a mixture of water and an ester, the hydrolysis of the ester proceeds at a greater velocity than it does when no catalyst is added. Between the two types of reaction, however, a distinction must be drawn; for in the case of the alkali, the base is progressively used up during the reaction owing to the formation of an alkali salt of the acid liberated from the ester; whereas in the case of the acid catalyst the phenomenon of auto-catalysis is observed, owing to the liberated acid beginning in its turn to play a catalytic part.

In the early days of the ionic theory of solutions, the catalytic influence of an acid was ascribed to the action of ions, the hydrogen ion being selected as the most active; and for a time this seems to have satisfied every one. But with further investigation, difficulties began to appear. For example, it was found that an N/2-solution of nitric acid inverted cane-sugar 6·07 times as fast as an N/10-solution did, although the ratio of the numbers of ions present are as 4·64 : 1. This goes to prove that the catalytic action is not directly proportional

[1] Sabatier, *La catalyse en chimie organique.*

Digitized by Google

to the number of hydrogen ions present; and it is now known that although in dilute solutions there appears to be a connection between the number of ions and the catalytic effect, the results deviate more and more from this state of affairs with increasing concentration of the acid.[1]

An even greater difficulty was found when the action of mixed acids and salts was examined. When to an acid there is added a salt yielding the same ion as the acid, it is found that the catalytic action of the mixture is greater than that of the acid alone. But on the ionic theory, the addition of the salt must reduce the ionisation of the acid and hence diminish the number of hydrogen ions in the solution. For instance, the velocity of hydrolysis of cane-sugar in presence of an N/20 solution of nitric acid is represented by 29·9. Theoretically, the addition of a certain proportion of potassium nitrate solution (0·04 N) should lower the velocity to 27·2; but in practice it is found to have the reverse effect, raising it to 33·9. Thus, although the ionisation of the acid is diminished, the catalytic effect is increased.

In order to escape from this difficulty, Arrhenius[2] brought forward the suggestion that the introduction of the salt plays a twofold part: in the first place it reduces the total number of hydrogen ions present; whilst in the second place it stimulates the activity of those remaining. Another form of explanation is arrived at by assuming that solvates are formed on the addition of the salt; and that owing to the withdrawal of water to produce these solvates, the concentration of the hydrogen ions in the rest of the system is increased.

The idea that the undissociated part of the salt has a catalytic action of its own is supported by the work of several investigators.[3] If it be accepted, then the velocity of a catalysed reaction can be regarded as the sum of two velocities which are determined respectively by the catalytic activity of the molecule and of the ion, each acting in proportion to its concentration. In the case of weak acid catalysts, the main activity resides in the ion; but with increasing strength of the

[1] Ostwald, *J. pr. Chem.*, 1885, **31**, 307.

[2] Arrhenius, *Zeitsch. physikal. Chem.*, 1889, **4**, 226.

[3] Senter, *Trans.*, 1907, **91**, 460; Lapworth, *ibid.*, 1908, **93**, 2197; Acree and Nirdlinger, *Amer. Chem. J.*, 1907, **38**, 489; Snethlage, *Zeitsch. Elektrochem.*, 1912, **18**, 589; *Zeitsch. physikal. Chem.*, 1913, **85**, 211.

Digitized by Google

acid, the undissociated molecule begins to play its part; until in the case of hydrochloric acid it is assumed that the ionic catalytic influence falls into the second place.

Applying this hypothesis to the facts given above, it will be found that it is quite in accordance with them. It accounts for the fact that when the concentration of a strongly acid catalyst is increased, the catalytic action becomes greater than the value calculated from purely ionic considerations; because with increase in concentration, more undissociated molecules are being brought into the solution. Again, the influence of neutral salts is explained on the assumption that by reducing the ionisation they bring into play the catalytic activity of the molecules of the acid instead of that of the ions.

Apart from a certain air of "heads-I-win-tails-you-lose" which is unavoidable in a case of this kind, the hypothesis appears to be satisfactory. It seems not improbable that in concentrated solutions there may occur some process akin to that of ionisation by collision which is known to take place in gases. If it be assumed that a collision between an ion and a molecule may in some circumstances produce a charged molecule which has a catalytic influence, the mechanism of the process becomes quite explicable; for such collisions will take place frequently only when the solution is a concentrated one; and the retention of the charge by a molecule would depend very largely upon the molecular character.

Radiant Energy and Chemical Reactions.—Perrin[1] has drawn attention to the relations between radiation and reactions in the following manner: In the case of a monomolecular reaction, he points out, a fixed fraction of the material present will be decomposed during unit time, provided that the temperature be constant. This rate of decomposition is unaffected by the presence or absence of molecules of another substance in the same vessel; and hence it follows that the molecular decomposition is entirely independent of collisions between two or more molecules. Whether an unstable gas be under high or low pressure, the same proportion of its molecules will break up during unit time; although in the one case there are frequent inter-molecular collisions whilst in the other the mutual impacts of molecules are few and far between.

[1] Perrin, *Les Atomes*, 1913, pp. 230 ff.

Digitized by Google

This seems sufficient to establish Perrin's thesis that the probability of breakdown in a molecule does not depend upon external shock. What, then, produces the "fragile" phase in a molecule's existence during which phase it is liable to decompose? In Perrin's view, since temperature has a very marked influence upon molecular stability, we must seek in this direction for the required explanation. Since temperature manifests itself through radiation as well as through molecular collisions, he believes that the origin of molecular dissociation is to be found in the light-waves which, whether visible or invisible, fill the space in which molecules move. As he puts it: "We must seek in an action of light upon atoms a mechanism which is essential to all chemical reactions".

Let us look at the matter from a slightly different point of view.[1] Oxygen and hydrogen exist side by side at ordinary temperatures without showing any inclination to combine with each other; but when the temperature is raised to 600° C., they unite with almost explosive violence. Now, on a purely kinetic basis, it can be calculated that the increase in the number of molecular collisions for a 10° C. rise in temperature is only 2 per cent., yet in the same range it is found that the velocity constant of the reaction more than doubles itself. Obviously some factor, other than mere molecular impact, is making its presence felt.

Arrhenius assumed that under any conditions the number of molecular impacts was sufficiently numerous to govern the velocity of chemical change; but he introduced the idea of "active" and "inactive" molecules, and made the hypothesis that an inter-molecular collision was effective only when an "active" molecule was concerned. He formulated the following expression:—

$$\frac{d \log K}{dT} = \frac{E}{RT^2}$$

to express the relation between the velocity constant of a reaction and the temperature. Here E is the energy required to convert one gramme-molecule from the inactive to the active condition. A similar expression was deduced by Marcelin[2] on the assumption that an inactive molecule passes into the active

[1] Arrhenius, *Zeitsch. physikal. Chem.*, 1889, **4**, 22; 1899, **28**, 317.
[2] Marcelin, *Compt. rend.*, 1914, **158**, 161.

Digitized by Google

state when its internal energy exceeds a definite critical value. On Marcelin's hypothesis, the factor E in Arrhenius' equation represents the extra amount of energy (over and above the average energy of the molecules) which must be supplied in order to bring about the change from an inactive to an active state. This relationship has been further investigated by Lewis,[1] but his work must be consulted in the original papers.

6. *Conclusion.*

In the space of a short chapter it has only been possible to draw attention to some of the most interesting points in connection with catalysis; and no attempt has been made to write a full account of the phenomena in this field.

Enough has been said, however, to show that here, as in the case of colloids, no single hypothesis seems capable of including all the known facts; and it appears probable that instead of working toward a comprehensive theory, it will be found advisable to seek in some division of the subject a better chance of arriving at an explanation of these puzzling phenomena. It is hardly possible to include under one head cases of intermediate compound formation and of ionic catalysis, even though electrical factors be assumed in both regions.

The industrial applications of catalysis are now so numerous that even the mere mention of them by name would occupy a chapter in itself. For information on this subject, the reader is referred to the works mentioned in the bibliography at the end of this volume.

[1] Lewis, *Trans.*, 1914, **105**, 2330; 1915, **107**, 233; 1916, **109**, 55, 67; 1917, **111**, 389, 457, 1086; 1918, **113**, 471.

Digitized by Google

CHAPTER XVI.

THE SPECTRA OF THE ELEMENTS.

1. *Introductory.*

THE application of the spectroscope to chemical problems is comparatively recent, since it was only from 1860 onwards that its possibilities were fully recognised; but even in that brief span it has proved itself one of the most powerful weapons in the hands of investigators. Caesium, rubidium, thallium, indium, gallium and five inert gaseous elements were all discovered by the aid of spectroscopic methods, which is sufficient to prove how valuable an adjunct to chemistry the spectroscope has become.

In the chemical applications of spectroscopy there are three main fields of interest: emission spectra, phosphorescence spectra and absorption spectra. The two former categories include cases in which light is emitted by the substance under examination, while absorption spectra are concerned with the nature of the light which a compound absorbs. The relation between visible colour and chemical constitution represents a branch of absorption spectroscopy, from which it may be seen how wide a field is covered by the subject.[1]

In the present chapter, only emission spectra and phosphorescence spectra will be described. But before dealing with them in detail it is desirable to define the meaning of certain terms which will be used later.

When a piece of iron is slowly heated, its rise in temperature is accompanied by certain changes in its radiation. At first, only the heat-rays of the infra-red region are emitted; then, as the temperature is raised, it glows dull red, showing that the red end of the spectrum has been reached; while further heating changes the colour of the iron through bright red up to

[1] For further information with regard to absorption spectra, reference may be made to Smiles, *Chemical Constitution and Physical Properties*, 1910.

Digitized by Google

white. Examination by means of the spectroscope will show that at each of these stages the iron is emitting a continuous series of radiations; for the spectrum appears as an unbroken band of light which extends further and further toward the ultra-violet as the temperature rises. This uninterrupted band of light varies in colour from point to point, of course; but it is apparently built up from a series of vibrations so complete that we can detect no break in the set. Such an unbroken series of vibrations is termed a *continuous spectrum.*

Now when nitrogen is placed in a vacuum tube and excited by means of an electrical discharge, its spectrum differs from that of a heated solid such as iron. Instead of the continuous band of light, the spectroscope reveals a series of flutings, almost like those on a Corinthian column illuminated from the side; and between the flutings there may be dark spaces. Careful examination with a powerful spectroscope brings to light the nature of these flutings. They are found to be groups of fine lines which are so arranged that they stand closer and closer together towards one or other end of the spectrum, so that finally they appear to run together in a single line which is called the head. The brightest part of the arrangement is obviously the region in which the lines approximate most closely to each other; and the brilliancy diminishes as the lines fall more and more apart towards the tail of the grouping. The fluted appearance is due to the presence in the spectrum of several such groupings, which produce an alternation of strong and faint areas in the strip of light. In some cases there are actual gaps in the spectrum where no lines at all occur, so that it is built up of several disconnected light-groups. Spectra which contain arrangements of this kind are known as *band spectra.* It should be noted that in the case of phosphorescence spectra it has not yet been possible to resolve the bands into lines; but there seems to be little doubt that the phosphorescence spectrum is essentially the same as an ordinary band spectrum.

Finally, there are other spectra in which the lines are so widely separated from each other that no banded structure is apparent; the spectrum takes the form of a series of brilliant lines upon a dark background. In this case we have what is called a *line spectrum.*

From what has been said above, it is evident that continu-

Digitized by Google

ous spectra offer little interest from the chemical standpoint. The difference between the spectrum of a mass of heated iron and that of heated lime is merely one of temperature and has nothing to do with the chemical characteristics of the two materials. Both, when raised to a white heat, emit the same spectrum. Line and band spectra, on the other hand, are closely connected with the nature of the material under examination; and each element when examined under uniform conditions emits its own characteristic spectrum. Not only so, but even the same element exhibits different spectra according to the manner in which it is excited.

2. *X-ray Spectra.*

The simplest spectra which have as yet been discovered are the X-ray spectra. X-rays have now been proved to be ordinary light in which the wave-lengths are extremely small, so that in the complete spectrum the X-ray region lies far beyond the ultra-violet.

When any material is bombarded with a stream of cathode particles in a Crookes' tube, it emits X-rays. These rays, owing to their extremely small wave-length, cannot be refracted or diffracted by ordinary prisms and gratings; but diffraction phenomena are observed when the rays are allowed to impinge upon crystals. Taking advantage of this behaviour, Moseley [1] investigated the character of the X-rays emitted when various elements were subjected to the cathode bombardment.

Owing to the fact that the crystal is a three-dimensional object whereas an ordinary diffraction grating is two-dimensional, the X-ray spectra are composed of fewer lines than the ordinary light spectra yielded by prisms or gratings. In general, the elements give rise to X-ray spectra containing two strong lines, along with other weaker ones which are related to them. Moseley discovered that the frequency (*i.e.*, the reciprocal of the wave-length) of a given line in the X-ray spectrum could be expressed by the formula—

$$\nu = A(N - b)^2$$

in which ν is the frequency, A and b are constants, and N is

[1] Moseley, *Phil. Mag.*, 1913, **26**, 1024; 1914, **27**, 703.

Digitized by Google

what is known as the Atomic Number of the element under examination.*

This example suffices to bring out two points. In the first place, there is something calculable in connection with spectral lines; and, secondly, there must be some general relationship between the spectra of all the elements, since a single formula suffices to express their characteristics.

3. *Flame Spectra.*

The spectra of volatile materials in flames are among the first phenomena which the student encounters in his analytical training, for the ordinary flame tests depend upon them; but when the matter is examined with proper precautions it is found to be by no means so simple as it appears at first sight. It must be remembered that a flame is not a uniform thing, but possesses a somewhat complex structure; and in consequence of this organisation, each of its different zones has a character of its own which exerts a certain influence upon spectroscopic work.

Examination of a Bunsen flame will show that it is composed of three main zones which are readily distinguishable from one another. In the very centre of the flame, just where it emerges from the jet, there is a blue cone. Superimposed upon this there is a greenish intermediate zone, more luminous than the blue cone. Finally, the main body of the flame is an outer zone which is almost non-luminous. The blue cone contains an excess of coal-gas and forms the reducing part of the flame; the intermediate zone is supposed to be a region in which the air and gas form an explosive mixture of a concentration such that the velocity of the explosion wave is exactly the same as the rate at which gas is issuing from the burner; the outer mantle of the flame contains a mixture of gas and air which varies in composition from centre to superficies, gas being in excess in the inner parts and oxygen in excess at the surface. This outer mantle forms the oxidising flame of the Bunsen.

It is quite evident that when a salt is introduced into such a flame, each of the three regions will exert a different influ-

* The term Atomic Number is explained on p. 339.

Digitized by Google

ence; and it is to be expected that the spectrum emitted from each region will differ from that of its neighbour. This can be shown to be correct in the following manner. Suppose that some potassium salt is introduced into the flame in order to colour it; and that the image of the flame is then projected by means of a lens upon the vertical slit of the spectroscope, care being taken that the whole length of the flame is on the slit at one time. When the spectrum is then examined, it will be found to consist of three horizontal regions of different characters: one corresponding to the blue cone, another to the intermediate zone and a third to the outer mantle. There is, of course, a certain overlapping of the effects; but the main characters of the various zones are clearly visible.

In the strip corresponding to the blue cone, all the lines of the potassium spectrum are detectable and in addition there appears what is known as the Swan spectrum, which may be due to the presence of hydrocarbons in the flame.* These two spectra appear upon a continuous background of light which may be the continuous spectrum produced by particles of carbon or unvolatilised fragments of the potassium salt in the flame.

In the second, intermediate, zone this continuous spectrum is not observed; nor is the metallic spectrum complete. Some of the potassium lines are missing.

The spectrum of the outer zone is found to contain only a few of the strongest potassium lines upon a completely dark ground.

This experiment is sufficient to show the complexity of even a simple "flame spectrum"; but a modification of the experimental conditions takes us a stage further forward. When various potassium salts are introduced into the flame, the lines characteristic of potassium are always shown; and when different sodium salts are employed, they all exhibit the D-line of the sodium spectrum. From this it seems evident that in the spectra of the flames we are observing the spectrum of the

* The cause of the Swan spectrum has not yet been satisfactorily explained. This particular spectrum is a band spectrum and it is observed in the inner cone of an acetylene flame, in vacuum tubes containing hydrocarbons, in spark discharges from carbon electrodes through moist air or hydrogen, in the cyanogen flame and in discharges through carbon disulphide, chloroform and carbon tetrachloride. It appears to be absent from the flames of carbon monoxide or carbon disulphide.

Digitized by Google

metal and not the spectra of the various compounds which are used. If for the alkali metals we substitute metals of the alkaline earths, it is found that the spectra differ from one another when a chloride is substituted for a bromide or an iodide; and from this behaviour it is inferred that the spectra observed here are those of the compounds and not of the elements.

In the case of gases, the spectra of compounds have been observed in not a few cases, *e.g.*, ammonia, cyanogen, and silicon tetrafluoride. As a whole, however, the subject has not been deeply studied.

4. *Reversion Spectra.*

In ordinary spectroscopic practice, when it is necessary to examine the spark spectrum of a dissolved substance, the negative pole of an induction coil is placed in the solution and the positive pole outside. In this case, the spark exhibits the spectrum of the solute quite normally. If, however, the electrodes be exchanged, so that the positive pole is placed in the solution and the negative electrode is brought very close to the surface of the liquid, then a new phenomenon is observed. The liquid in the neighbourhood of the spark glows visibly in the case of some solutes, especially salts of the rare earth group. Owing to the inversion of the usual procedure in this case, these spectra are termed *reversion spectra.*

The spectra thus observed are band spectra. In dilute solutions, the spectrum is almost entirely independent of the nature of the acidic radicle in the salt; but concentrated or strongly acidic solutions show a different spectrum which is supposed to be that of the undissociated salt.

5. *Phosphorescence Spectra.*

When some solids are subjected to the cathode bombardment in a Crookes' tube they emit light; and examination shows that the spectrum thus produced is a band one. It is possible to draw up certain general rules to which the majority of the phenomena conform, though these rules are not rigidly applicable in every case.

The cathodic phosphorescence is not a general property of

Digitized by Google

matter, for certain materials show no trace of light-emission when subjected to the cathode discharge. Among these non-phosphorescent substances, however, some are found which, while showing no activity when pure, are capable of exhibiting phosphorescence in presence of traces of impurities. Also, some compounds which show phosphorescence when apparently pure have the power of light-emission very much increased by the addition of a trace of impurity; and the character of the light which they throw out may be markedly affected by the nature of the impurity added. Thus zinc sulphide, when prepared in a special way, shows a green phosphorescence under the cathode rays; with the addition of a trace of bismuth salts, the tint of the emitted light alters; and when the impurity is a trace of manganese, the light changes to golden-yellow or even orange.

The general effect of impurities may be described as follows: Suppose that a certain substance A is non-phosphorescent when pure but acquires the power of phosphorescence by the addition to it of a trace of B. As the proportion of B present in the mixture is increased, the phosphorescence becomes stronger until a maximum is attained. Beyond this, further addition of B leads to a weakening of the phosphorescent power. In general, the percentage of B which gives the maximum phosphorescence is 0·5 per cent. to 1 per cent. An increase in the proportion of B to 20 per cent. may entirely extinguish the phosphorescence.*

If B is a compound of one of the rare earth elements, the phosphorescence spectrum may be a discontinuous one; but each of the bands composing this discontinuous spectrum obeys the above law of maximum composition. The most refrangible bands—those at the violet end of the spectrum—reach their maximum brightness with smaller percentages of B than are required to influence the red bands; hence, as the percentage of B present increases from zero upward, the colour of the phosphorescence, as seen by the naked eye, usually passes from the violet toward the red.

* Compare with this the gradual increase to a maximum and subsequent decrease in illuminating power which is found when the percentage of cerium in an incandescent gas mantle is raised. The light from a mantle containing 99 per cent. thorium and 1 per cent. cerium is about seven times as bright as that of a mantle containing pure thorium,

Digitized by Google

The compound B is generally termed the phosphorogen and the compound A is known as the diluent.

It appears probable that cathodic phosphorescence is intimately connected with the presence of a solid solution. For instance, if zinc sulphide be prepared by precipitating a solution of a zinc salt containing a trace of a manganese salt, the dried precipitate shows no sign of phosphorescence under the cathode discharge; but if the precipitate be heated in an electric furnace for a certain time, the material will be found to have acquired the power of emitting a golden light under the action of the cathode rays. Evidently a mere mixture of zinc and manganese sulphides is not sufficient; the two must be heated together: and in this heating it is supposed that a solid solution of the manganese sulphide in the zinc sulphide is produced.

A practical application of phosphorescence spectra is to be found in the identification of elements of the rare earth group, since the merest trace of the phosphorogen suffices for an examination and the spectrum is characteristic of the element present as an impurity. Pure lime is used as the diluent. A great advantage of phosphorescence spectra is due to the fact that they contain no "air lines" nor do they show lines due to the elements of the electrodes.

6. *Arc Spectra.*

Owing to the comparatively low temperatures of even the hottest flames, it is impossible to volatilise many substances by means of a flame; so that in order to examine the spectra of these materials recourse must be had to the electric arc. Various methods are employed, such as using electrodes of the substance to be examined, or by filling the core of a hollow electrode with a salt of the metal or by saturating carbon electrodes with a solution of the salt and allowing them to dry before use or by placing some of the salt in a hole at the end of the electrode.

However the arc spectrum be obtained, it is found to be much more complex than that which is observed in the case of a flame. The spectrum of an arc between iron electrodes, for example, contains some two thousand lines.

Digitized by Google

Univ. of California

Digitized by Google

FIG. 30.—Portion of Iron Arc Spectrum showing different lengths and thicknesses of lines.
From Baly's "Spectroscopy". [*To face p.* 281.

Digitized by Google

When the arc spectrum of a metal is examined, a striking peculiarity of the lines is revealed. Fig. 30 shows a portion of the arc spectrum of iron. It is evident that the "lines" in this are not uniform either in length or in thickness; and the larger ones can be seen to exhibit cigar-shaped outlines. Consideration will show the meaning of the differences in length. Suppose that the arc image is focussed so that the horizontal arc is at right angles to the vertical slit of the spectroscope and that the image of the arc has a diameter exactly equal to the length of the slit. Then in the case of a long line in the spectrum it is clear that the material giving rise to this line must have extended right across the arc from top to bottom, since traces of it appear over the whole slit. In the case of a short line, on the other hand, the two ends of the slit are evidently producing no image on the photographic plate; and only the middle portion of the slit is lit up by this particular light. This clearly implies that the material giving rise to this line does not extend right through the arc, but is confined to its central portion. Now the central core of the arc is obviously hotter than the outside zone; so that the short lines are produced only in the hottest zone of the arc whilst the long lines are emitted by both hot and colder parts of the arc. Whence we may reasonably infer that the long lines correspond to a material at a temperature lower than that of the substance which produces the short lines. In other words, in the case of a mixture, the longest lines would be those of the more volatile of the two components, whilst the short lines would be those of the less volatile component which could only be vaporised in the hot core of the arc.

In the spectrum in Fig. 30, however, there is no question of a mixture, since the only substance present is the element iron; and we are thus driven to conclude that the difference in the length of the lines corresponds to a difference in state of the element in the centre and at the edge of the arc. In other words, the spectrum of iron depends upon the temperature at which it is examined.

With regard to the second factor, the breadth of the lines, it is found that an increase in pressure of a gas tends to broaden the lines in the gas's spectrum; so it appears

Digitized by Google

that the breadth of the lines may be related to the density of the gas which produces them.

7. *Spark Spectra.*

When, instead of an arc discharge, an electric spark from an induction coil is passed between two metallic electrodes, a line spectrum is produced which at first sight appears very similar to that of the arc. Closer examination reveals an apparent increase in the number of the lines; but a careful comparison between arc and spark spectra shows that this increase is not a real one. Most of the lines in the spark spectrum can be traced also in the arc spectrum; but in the spectrum of the arc some of them are so short as to be hardly noticeable.

Thus the main difference between the arc and spark spectra is to be found in the fact that the spark spectrum contains lines of a length greater than the corresponding lines in the arc spectrum. These lines which increase in length as we pass from arc to spark are termed *enhanced lines.*

Taking into consideration the facts given in the previous section as to the connection between length of line and temperature, it might be assumed that the electric spark is very much hotter than the electric arc. There is no evidence against this view; but it is well to be cautious and to bear in mind that the electrical state of affairs in the spark is widely different from that in the arc; and this difference in conditions might suffice to account for the difference in the spectra, without any temperature effect coming into play at all.

8. *Regularities in Line Spectra.*

Though at first sight the spectra of elements appear to contain a number of lines in completely irregular distribution (see Fig. 30), closer examination reveals the fact that definite relationships can be traced in some cases between the different vibrations, so that the spectra actually display certain regularities.

The simplest relationship is found in cases where there

Digitized by Google

is a constant difference between the oscillation frequencies * of certain lines. If ν_1, ν_2, ν_3, etc., be the frequencies of three different lines in a spectrum, this relation is expressed by—

$$\nu_1 - \nu_2 = \nu_3 - \nu_4 = \nu_5 - \nu_6$$

For example, in the spectrum of magnesium there are lines having the frequencies shown below :—

(I.)	(II.)	Difference.
1928·9	2606·0	677·1
1932·9	2609·9	677·0
1934·5	2611·9	677·4

Thus the corresponding lines in columns (I.) and (II.) differ from each other by 677 units.

The second type of relationship between spectral lines is more complex. It is found that some spectra contain sequences of lines diminishing in intensity as the wave-length increases and related to one another in a manner which can be expressed in a mathematical formula. The first successful attempt to group these *series*, as they are called, into a common arrangement was made by Balmer,[1] who showed that the positions of lines in the hydrogen spectrum could be calculated with considerable accuracy by means of the formula—

$$\lambda = A \frac{m^2}{m_2 - 4} \times 10^{-6} \text{ cms.}$$

Here λ is the wave-length of the line; A is a constant equal to 3645 for all the lines of the hydrogen series; and m is one of the integers in the series 3, 4, 5.

More accurate results are obtained by the use of other formulæ suggested by Kayser and Runge [2] and by Rydberg.[3] The former investigators used the following expression :—

$$\nu = A + Bn^{-2} + Cn^{-4}$$

wherein ν is the oscillation frequency of the line; n is a whole number in the series 3, 4, 5 . . .; and A, B and C

[1] Balmer, *Ann. d. Physik*, 1885, **25**, 8.
[2] Kayser and Runge, *ibid.*, 1890, **41**, 302.
[3] Rydberg, *Zeitsch. physikal. Chem.*, 1890, **5**, 227.

* The oscillation frequency is the reciprocal of the wave-length.

Digitized by Google

are constants calculated for each particular spectral series. Rydberg's formula is—

$$\nu = n_o - \frac{N_o}{(\mu + m)^2}$$

in which ν is the oscillation frequency of the line; m is an integer of the series 1, 2, 3 . . .; n_o and μ are characteristic constants differing from spectral series to spectral series; whilst N_o is apparently a universal constant having the value 109675 and applicable to all series. The discovery of Rydberg's constant makes his work of more general importance than that of Kayser and Runge.

These formulæ enable us to determine the positions of all the lines belonging to a single spectral series in a given spectrum; and by their aid it is possible to sort out from an apparently irregular grouping of lines two or three perfectly regular, independent series, the superposition of which produces the apparent confusion in the complete spectrum.

In view of the complexity of certain line spectra, it might be suggested that in their case agreement with the formulæ is less surprising than non-agreement would be, since the lines are so closely placed that almost any formula would find one set of lines which would agree with it. There is, however, satisfactory experimental evidence that the lines of a spectral series are physically and not merely mathematically related to one another; and it may be well to give a short description of this.

When a light-source is placed in a powerful magnetic field it is found in some cases that the spectrum of the source is altered. For example, when the magnet is not in action, the spectrum may show a single line in a particular position. On switching on the magnet and examining the spectrum with the spectroscope at right angles to the magnetic field, the original single line is found to be split up into three components. Viewed through a hole running through the two pole-pieces of the magnet, two lines are seen instead of the original single line. This phenomenon is known as the Zeeman effect, after its discoverer.[1]

[1] Zeeman, *Phil. Mag.*, 1897, **43**, 226.

Digitized by Google

The cause of the Zeeman effect is the action of the magnetic field upon the electrons within the atom; and it is evident that if several lines in a spectrum show identical Zeeman phenomena, these lines must have a common origin in some part of the intra-atomic machinery which is influenced by the magnet. Now it has been found experimentally that if one of the lines in a spectral series is duplicated by the action of a magnetic field, all its congeners in the same series suffer exactly the same change; * which shows conclusively that there is some physical relation between them.

Further, if one of the lines in a spectral series is broadened by the application of heavy pressure to the gas emitting the spectrum, all the other lines of the same series are also broadened.

Again, when the method of producing the spectrum is changed, it is found that all the lines in a given series are either brightened or dimmed by the change in method.

This evidence appears to furnish conclusive proof that the spectral series are not mere mathematical coincidences but actually represent sets of vibrations which have a common origin or at any rate are physically related to each other.

9. *Line Spectra and the Periodic System.*

When the spectra of the elements are compared, it is found that there is a rough resemblance between the spectra of members of the same sub-group of the Periodic Table. Thus lithium, sodium, potassium, rubidium and caesium show a kinship in their spectra, whilst copper, silver and gold form another group of inter-related materials. The discoverer of this relationship was Lecoq de Boisbaudran,[1] who pointed out that within the same class of elements the spectra resembled each other in general character but that with an increase in atomic weight there was a shifting of the whole spectrum towards either the red or violet. This observation he utilised in the case of gallium, which he discovered shortly afterwards. Having only a very small quantity of the element at his

[1] Lecoq de Boisbaudran, *Ann. Soc. Sci. nat. Charente-Inférieure*, 1870.

* This is known as Preston's Law. It does not hold good in the case of helium, but in general it appears to be correct.

Digitized by Google

disposal at first, he was unable to determine its atomic weight by chemical methods; but on applying the spectroscope, he noticed two characteristic lines in the violet. Comparing these lines with the corresponding lines in the aluminium and indium spectra, he calculated the approximate atomic weight of gallium from the relations between the three pairs of lines; and in this way [1] he obtained a value which was astonishingly near the mark (69·86 instead of 69·9).

In spite of this surprising success, the relationship in elemental spectra is not so simple as Boisbaudran supposed. The ratio of atomic weight to line wave-length is not by any means constant; and sometimes it is found that a single line in the spectrum of one element corresponds to a group of lines in the spectrum of another, which introduces a certain arbitrary factor into the calculations. Evidence in general support of the hypothesis is found in the work of Ditte, Trooste and Hautefeuille.[2]

In more recent times, attempts have been made to connect the oscillation frequencies in the elemental spectra with the atomic weights.[3] It has been shown that there is an approximate relationship between the square of the atomic weight of an element and the frequency difference between doublet or triplet lines in the spectrum. The following table, given by Rydberg, shows the general relations between the elements in some Groups; A represents the atomic weight of the element and ν the frequency differences between corresponding pairs of lines in the elements of the same Group. The value of $10^3\nu/A^2$ is printed in heavy type in each case, and it will be seen that it is approximately constant for the members of a single Group:—

[1] Lecoq de Boisbaudran, *Compt. rend.*, 1875, **81**, 1100; *Ann. chim. phys.*, 1877, **10**, 100; see also the article Gallium in Wurtz' *Dictionnaire de chimie*, Supp. II., 859.

[2] Ditte, *Compt. rend.*, 1871, **73**, 622, 788; Trooste and Hautefeuille, *ibid.*, **77**, 620.

[3] See Rydberg, *International Reports, Paris*, 1900, **2**, 217; Runge and Precht, *Zeitsch. Elektrochem.*, 1904, **10**, 119; *Physikal. Zeitsch.*, 1903, **4**, 285; Ramage, *Proc. Roy. Soc.*, 1902, A, **70**, 1, 303; Watts, *Phil. Mag.*, 1903, **5**, 203.

Digitized by Google

	Sodium.	Magnesium.	Aluminium.	Oxygen.
$\nu =$	17·9	40·91	112·02	3·70
$10^3\nu/A^2 =$	32·3	68·8	152·8	14·5
	Potassium.	Calcium.	Gallium.	Sulphur.
$\nu =$	57·85	105·82	823·6	18·15
$10^3\nu/A^2 =$	37·8	66·1	168·6	17·17
	Rubidium.	Strontium.	Indium.	Selenium.
$\nu =$	235·98	394·22	2212·54	103·7
$10^3\nu/A^2 =$	32·3	51·5	172·1	16·6
	Cæsium.	Barium.	Thallium.	
$\nu =$	553·87	878·5	7792·63	
$10^3\nu/A^2 =$	31·6	46·8	187·0	

Rydberg has also pointed out that a periodic curve is produced by plotting the values of $10^3\nu/A^2$ against the atomic weights.

It is curious that up to the present, no one seems to have compared the atomic numbers with the line differences. When this is done, it appears that there is a much closer relationship traceable between these two functions than is detectable between line differences and atomic weights. If there be any relationship between the quantities, it is most easily detected in the following way:—

Assume that the frequency differences D vary (*a*) with the m^{th} power of the atomic weight A or (*b*) with the n^{th} power of the atomic number N. We then have the following expressions:—

$$(a) \quad D = A^m \qquad (b) \quad D = N^n$$

and

$$m = \frac{\log D}{\log A} \qquad n = \frac{\log D}{\log N}$$

Then throughout the Group, the values of m or n should remain constant; and whichever is the more nearly constant of the two represents the closer relationship to the line differences.

The following differences in oscillation frequency between corresponding pairs of lines in the spectra of the various elements in two groups may be used in calculation; and in each case the value of m and n are given in the corresponding columns:—

Digitized by Google

	Differences.	$m = \frac{\log D}{\log A}$.	$n = \frac{\log D}{\log N}$.
Magnesium	91·5	1·41	1·81
Calcium	223·1	1·46	1·80
Strontium	801·4	1·44	1·88
Barium	1691·1	1·51	1·85
Radium	4858·6	1·56	1·89
Sodium	179	1·67	2·16
Potassium	578	1·73	2·16
Rubidium	2360	1·79	2·15
Caesium	5539	1·76	2·15

Examination of the figures will show that the value of log D/log A varies between 1·41 and 1·56 in one series and between 1·67 and 1·79 in the other, or approximately 10 per cent.; whereas the value of log D/log N varies by 5 per cent. at most in the Magnesium Group and by only 1 per cent. in the Sodium Group.

From this it seems evident that a much closer relationship exists between the atomic numbers and frequency differences than between atomic weights and differences. The same point is brought out graphically by plotting the logarithms of the atomic numbers as abscissæ and the logarithms of the frequency differences as ordinates, in which case all the points in one Group lie upon straight lines.

Digitized by Google

CHAPTER XVII.

CHEMICAL AFFINITY.

1. *Introductory.*

CHEMICAL affinity may be regarded in either of two ways, as a property or as a force. On the first assumption, it is the property possessed by bodies in virtue of which they are capable of entering into chemical reaction with certain other bodies when contact is established. On the second assumption, it is the force which draws together two materials capable of chemical interaction and produces from them new substances having properties different from those of the parent bodies. It is evident that these two definitions do not mean exactly the same thing: for the first of them implies that chemical affinity is something residing in the atom apart altogether from its surroundings; whilst the second definition carries with it the implication that at least two bodies are necessary before affinity can come into existence. The difference between the two can be most easily seen by means of a simple analogy. If a helium atom were entirely isolated in space, could we reasonably speak of gravitation in connection with it? It has nothing around it which it could attract or which could be attracted by it, so that it can display no gravitational properties: nevertheless, as soon as a second helium atom is brought into the neighbourhood, the two will be drawn toward each other. Upholders of the first definition would say that the helium atom possessed the potentiality of gravitation even under the first circumstances; whilst supporters of the second definition would maintain that only the coming of the second helium atom produced anything which could be called a gravitational effect. In the same way, it may be asked whether an isolated sodium atom possesses anything which can be properly termed chemical affinity or whether this

Digitized by Google

affinity only comes into existence when, say, a chlorine atom is brought into the neighbourhood of the sodium one.

Whichever of the two definitions be chosen, it will be found that only the vaguest conception of chemical affinity can be derived from it; and it is natural to go a step further in order to see whether more light can be thrown upon the subject. In nature there appear to be two categories under which chemical affinity might be placed. Gravitation, as far as we know it, is a unitary force; for under normal conditions we know nothing which could be ascribed to "negative gravitation". Electricity, on the other hand, exhibits a dualism, since we find positive and negative charges. Are we to rank our chemical affinity along with unitary gravitation or place it in the same category as electricity?

Berthollet[1] was the most prominent adherent to the unitary hypothesis. On his view, chemical affinity is a phase of gravitational energy; and the complexities of chemical problems (as compared with the simplicity of gravitational ones) are to be ascribed to the close proximity of the interacting substances. Owing to the extremely minute distances separating atoms from each other, influences come into play which are negligible in the case of gross masses: the form of molecules, the distances between them, the peculiar conditions under which they exist, all these tend to obscure the problem and make it very much more difficult to attack mathematically.

The dualistic hypothesis of chemical affinity was championed by Berzelius[2] and was developed by him into his electrochemical system. He assumed that each atom possesses two poles, one positive, the other negative; and these two poles carry unequal charges. If the positive charge preponderates over the negative one, the atom is positive in character; and it has a tendency to combine chemically with negative atoms. Thus every compound is built up from simpler groupings bearing opposite charges.

It is unnecessary to describe the historical development of our views on chemical affinity, as they have been fully dealt

[1] Berthollet, *Essai de Statique chimique*, 1803.

[2] Berzelius, *Schweigger's Journal*, 1812, 6, 119; *Lehrbuch d. Chemie*, Vol. I., part 1, 1827.

Digitized by Google

with in various works [1]; and in the remainder of this chapter attention will be confined to some of the more recent suggestions which have been put forward to account for the phenomena of chemical reactions. The selection has been made with a view to illustrating different standpoints rather than with any idea of weighing one view against another. In the main, the reader is expected to bring his own critical faculty to bear upon the problems suggested by the various authors.

With this aim of illustration in view, it has been thought best to select specimens of the following conceptions: (1) "directed affinities" which are supposed to act from the surface of the atom in definite directions or from fixed points on the atomic superficies; (2) "undirected affinities" which resemble gravitational forces in that they act outward from the centre of the atom in all directions; (3) electrochemical ideas; (4) polar and non-polar conceptions; and (5) purely electronic views of valency. These fundamental conceptions by no means exhaust the possibilities; but they will suffice to show how very different are the interpretations of the phenomena of atomic attraction.[2]

[1] Meyer, *History of Chemistry*, 1906; Armitage, *History of Chemistry*, 1906; Hilditch, *Concise History of Chemistry*, 1911; Pattison Muir, *Chemical Theories and Laws*, 1907; Freund, *Study of Chemical Composition*, 1904; Friend, *Theory of Valency*, 1909.

[2] The following list includes the chief papers on the subject but it is by no means a complete one: Wunderlich, *Konfiguration organischer Moleküle*, 1886; Auwers, *Entwicklung d. Stereochemie*, 1890; V. Meyer and Riecke, *Ber.*, 1888, **21**, 946; Wislicenus, *ibid.*, 1890, **23**, 477; Sachse, *ibid.*, 1888, **21**, 2590; Vorländer and Mumme, *ibid.*, 1903, **36**, 1470; Sachse, *Zeitsch. physikal. Chem.*, 1893, **11**, 185; Fry, *ibid.*, 1911, **76**, 385, 398, 591; 1912, **80**, 29; 1913, **82**, 665; Falk and Nelson, *J. Amer. Chem. Soc.*, 1910, **32**, 1637; *ibid.*, 1914, **36**, 209; Falk, *ibid.*, 1911, **33**, 1140; 1912, **34**, 1041; Nelson, Beans and Falk, *ibid.*, 1913, **35**, 1810; Fry, *ibid.*, 1908, **30**, **34**; 1912, **34**, 664; 1914, **36**, 248, 262; Erlenmeyer, *Annalen*, 1901, **316**, 71; Vorländer, *ibid.*, 1903, **320**, 99; Knorr, *ibid.*, 1894, **279**, 202; Knoevenagel, *ibid.*, 1900, **311**, 194; Vaubel, *Chem. Zeit.*, 1897, **21**, 96; de Heen, *Bull. Acad. Roy. Belg.*, **1904**, 285; Le Bel, *Bull. soc. chim.*, 1890, **3**, 788; Werner, *Beiträge z. Theorie d. Affinität u. Valens*; van't Hoff, *Lagerung d. Atome im Raume*; *Arrangement of Atoms in Space*; Friend, *Theory of Valency*; Kauffmann, *Valenzlehre*; Werner, *Neuere Anschauungen auf d. Gebiete d. anorgan. Chemie*; *Ber.*, 1907, **40**, 15; *Annalen*, 1912, **386**, 1; Spiegel, *Zeitsch. anorgan. Chem.*, 1902, **29**, 365; Arrhenius, *Theories of Chemistry*; Friend, *Trans.*, 1908, **93**, 260, 1007; 1916, **109**, 715; Briggs, *ibid.*, 1908, **93**, 1564; Ramsay, *ibid.*, 774; J. J. Thomson, *Corpuscular Theory of Matter*, 1907; Fry, *Electronic Theory of Valence*, 1921.

Digitized by Google

2. *Hypotheses of Directed Affinity.*

Before the development of stereochemistry, there was no necessity to consider the space relations of valency at all; but when chemical formulæ emerged from two into three dimensions, it was evident that the action of chemical affinity required a tridimensional symbolism if touch were to be maintained between theory and practice. The first step in this direction was taken by van't Hoff[1] whose conception was "a continuation of Kekulé's law of the quadrivalence of carbon, with the added hypothesis that the four valencies are directed towards the corners of a tetrahedron, at the centre of which is the carbon atom".

As chemical symbolism grew more and more mechanical under the impetus of stereochemical research, this conception of van't Hoff ceased to be in harmony with current ideas. On the assumptions of ordinary dynamics, it is possible to conceive forces acting along definite lines (provided that we are not concerned with the simultaneous action of two such forces) without coming into conflict with the chemical evidence in the case. But though the ideas of van't Hoff can be applied satisfactorily when only single bonds are concerned, it leads to dynamical impossibilities in the cases of the double and triple linkgaes of carbon. For example, in the ethylene derivatives the valencies would be arranged in the manner shown below:—

wherein forces are depicted as acting from two points and making an angle in space instead of operating along the straight line joining the two points.[2] If, instead of the two separate forces acting from each carbon atom, we assume a single resultant force, then we should have the same kind of system as in the single bond; and the occurrence of ethylenic stereoisomers such as maleic and fumaric acid would be impossible on the hypothesis, owing to free rotation of the two carbon atoms about their common axis.

It is obvious that the assumption of valencies acting in

[1] van't Hoff, *The Arrangement of Atoms in Space*, 1898, pp. 2-3.

[2] Auwers, *Entwicklung der Stereochemie*, 1890, p. 22; Lossen, *Ber.*, 1887, 20, 3306.

Digitized by Google

definite directions cannot be sustained, since it involves dynamic impossibilities; and it is necessary to seek some way out of the difficulty. The simplest suggestion consists in the idea that chemical affinity is situated on certain definite portions of the atomic surface; but there are various ways in which this requirement can be fulfilled.

Imagine, for example, that the four concentrations of affinity in the carbon atom are accumulated at the corners of a tetrahedron and that the atom itself is represented by a sphere circumscribed about the tetrahedron.[1] When a carbon atom is united to a monovalent atom by a single bond, we may symbolise the process by laying two affinity concentrations together, as in Fig. 31. Here the fourth affinity-centre of the carbon atom is supposed to lie above the plane of the paper. It will be seen that in this way the two mutually attracting affinity-centres are

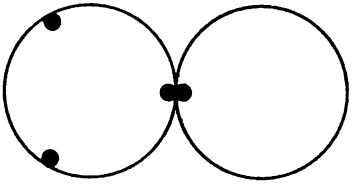


FIG. 31.

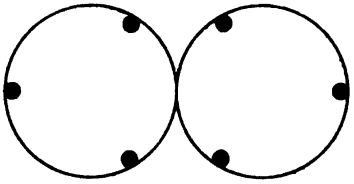


FIG. 32.

able to act directly upon one another and the pull of each upon the other is at its maximum. This represents the strong single bond, such as is found in ethyl chloride.

To represent the double bond between two carbon atoms, two affinity-centres in each atom have to be brought into positions of mutual attraction, as is shown in Fig. 32. Here, although the attracting forces are twice as strong as in the last case, the distance separating the attracting centres is much greater; and consequently the total pull between the two atoms will be weaker than before. This represents the comparatively feeble double linkage of ethylene.

In the case of the triple bond, three of the affinity-centres will be attracting each other; but they will be even further separated from each other in space: so that the weakness of the triple acetylenic bond is thus symbolised.

[1] Meyer and Jacobson, *Lehrbuch d. organ. Chemie*, first edition, Vol. I.

Digitized by Google

This mechanical representation of chemical affinity has its advantages; but it suffers from defects which make it difficult of acceptance. For example, there is no reason why, if the affinity-centre of one carbon atom attracts the affinity-centres of another atom, it should not equally attract its fellows on the same atom, so that they would tend to flow together over the surface. There seems to be no method of rendering their fixity probable upon mechanical assumptions.

To avoid this objection, V. Meyer and Riecke[1] devised a symbolic representation of affinity which is not without interest. They assume that the carbon atom is surrounded by an ethereal envelope of spherical form. The atom itself is regarded as the origin of specific affinity but the actual seat of its valencies is to be found in the ethereal shell's surface. Each valency is produced by the presence of two opposite electrical poles lying at the ends of a line which is short in comparison with the diameter of the ethereal envelope. The mid-points of these "dipoles" are fixed at the surface of the ethereal layer; but each "dipole" can swing freely about this fixed point.

This hypothesis accounts for the following: First, the tetrahedral grouping of atoms around a carbon atom is explicable since in their normal positions the four dipoles would naturally group themselves in the most symmetrical manner on the surface of the ethereal envelope—*i.e.*, at the corners of an inscribed tetrahedron. Second, in the case of certain compounds a deviation from this grouping is required which can be accounted for by a displacement of the dipoles. Third, the fact that there is an attraction between the affinities of two different atoms but no attraction between the affinities of the same atom is explicable on this hypothesis owing to the arrangement of the dipoles. Figs. 33 and 34 show the two possible representations of the single bond between two atoms and also the double bond. It will be seen that in the double bond, no free rotation of the two atoms about a common axis is possible. In the case of the single bond, one arrangement permits free rotation whilst another arrangement holds the atoms in a fixed position. This latter grouping would suffice to account for the existence of a third form of malic acid which

[1] V. Meyer and Riecke, *Ber.*, 1888, **21**, 946, 1620.

Digitized by Google

is not provided for by current theories, though it undoubtedly exists in nature.[1]

On the whole, however, mechanical conceptions of the action of chemical affinity such as these are not sought after at the present time. The relative decline in interest in stereochemical problems, which for some reason or other has taken place, has tended to throw into the background of chemical thought the concrete representations of valencies which were sufficiently numerous in the nineties of last century; and the newer trend appears to be in the direction of more fluid conceptions of chemical affinity.

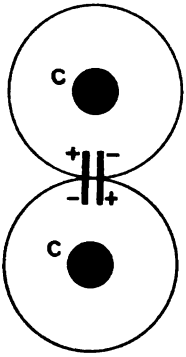


FIG. 33.
Single bond, free rotation.

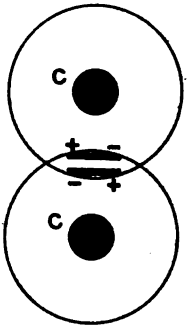


FIG. 34.
Single bond, no free rotation.

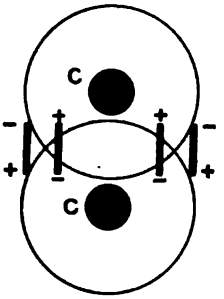


FIG. 35.
Double bond, no free rotation.

3. *Werner's Hypothesis.*

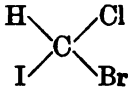
Le Bel[2] appears to have been one of the first modern chemists to regard valency as an "undirected force". His view was essentially dualistic, for he assumed that when atoms approached within a certain distance they became subject to a force of repulsion which overcame the chemical affinity drawing them together; so that eventually some of them took up positions upon the surface of a sphere surrounding a central atom. In this way, Le Bel was able to account for the tetrahedral grouping of atoms around a carbon atom which is demanded by stereochemical evidence.

[1] Aberson, *Verh. K. Akad. Wetensch. Amsterdam*, 1898; *Ber.*, 1898, **31**, 1432; Walden, *ibid.*, 2706.

[2] Le Bel, *Bull. soc. chim.*, 1890, **3**, 788.

Digitized by Google

A year later, Werner[1] put forward the germs of an hypothesis which he eventually developed into a most complicated system. Dropping Le Bel's conception of repulsion, Werner adopted the idea of spherical atoms and assumed that these atoms could actually come into contact at certain points, so that further approach was then stopped. He seems to have borrowed his ideas of valency from Claus[2] and Lossen,[3] so that in its earlier stages his hypothesis appears to have presented nothing particularly new. He assumed with Claus that each atom has a general store of valency which can be drawn upon to different extents by different atoms, so that, *e.g.*, the four "bonds" in the case of the compound—



would each have a strength different from the other three. He further assumed that a carbon atom cannot combine with more than four other atoms. When four atoms combine with a carbon atom, on his hypothesis, they arrange themselves on the surface of the carbon atom in such a way that each of them absorbs the maximum possible quantity of valency without interference with the other three atoms, the valency-force being assumed to act uniformly from the centre of the atom in all directions. In the case of methane, this implies that the four hydrogen atoms arrange themselves at the corners of a regular tetrahedron. Differences in the strengths of chemical attraction, Werner depicts as differences in the areas on the superficies of the carbon atom which are used by the various atoms to which it is attached.

This hypothesis, if containing nothing particularly new, at least served to produce a concrete, mechanical idea of atomic union; and some of the extensions of it to the case of the double bond between carbon atoms had a considerable ingenuity. It has certain inherent weaknesses, however, which cannot escape examination. If the usual values deduced for atomic volumes be correct, then the iodine atom is much larger than the fluorine atom. When attached to carbon, therefore, it

[1] Werner, *Beiträge z. Affinität u. Valenz*, 1891.
[2] Claus, *Ber.*, 1881, **14**, 432.
[3] Lossen, *Annalen*, 1886, **204**, 327; *Ber.*, 1887, **20**, 3306.

Digitized by Google

should exert its influence over a much wider superficies than the fluorine atom does; and therefore methyl iodide should be more stable than methyl fluoride, which is not the case. Again, on Werner's assumptions, affinity is a uniformly distributed force; yet in his later papers we find glib references to electrons, without any attempt being made to harmonise these two very antagonistic ideas in the field of valency. In its simple form, Werner's hypothesis never secured a firm footing among chemical theories; which makes it all the more extraordinary that many chemists accepted almost without examination the much more complicated superstructure which he built up on the original basis.

The second stage of Werner's development of valency conceptions seems to have been entirely his own.[1] It originated in the field of the complex salts and especially in the course of investigations upon the cobaltammines which have been described in an earlier chapter of this book; but even in this region it met with prolonged and well-devised resistance from Jörgensen who, before Werner began his work, was the greatest expert on the subject.* The vicissitudes of Werner's hypothesis were so varied that in the end it became difficult to be sure which parts of it remained as in the original statement of it and which ones had been jettisoned by its author, either openly or tacitly, in order to get out of the difficulties in which he found himself involved. Under these circumstances it is not easy to provide a fair summary of its somewhat elastic provisions.

Werner assumed that there were two types of valency: main valencies and auxiliary valencies. The exact difference between the two was defined by him in so many different ways that it is hard to give a clear idea of it; but for the present purpose the following will suffice.[2] "Main valencies and

[1] For an account of this hypothesis see Werner, *Ber.*, 1907, **40**, 15, or his *Lehrbuch d. Stereochemie*, 1904.

[2] Werner, *Lehrbuch d. Stereochemie*, p. 318, 1904.

* Before coming to any decision for or against the Werner hypothesis, the reader should consult the papers of Jörgensen (*Zeitsch. anorgan. Chem.*, 1894, **5**, 147; 1897, **13**, 172; **14**, 404; 1899, **19**, 109) and Petersen (*Zeitsch. physikal. Chem.*, 1902, **39**, 249). Whether Werner was right or wrong in his ideas, his handling of evidence seems to have been marked by a certain lack of scruples which is rare in scientific work.

Digitized by Google

auxiliary valencies are actions of affinity which apparently differ only in order of magnitude, like a metre and a part thereof. The standards of measurement of them are the electrons, in the sense that every action of affinity which is capable of receiving the action of electricity or appears to be equivalent to one which is thus capable, is called a main valency; whereas those actions of affinity which are neither so gifted nor equivalent with others so gifted, are termed auxiliary valencies. A molecular compound is thus to be regarded as a compound which has arisen through the simultaneous saturation of the main and auxiliary valencies of an elementary atom."

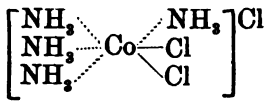
Divested of its cumbrous phraseology, this seems to mean that main valencies were those which are expressed by lines in ordinary graphic formulæ, whilst auxiliary valencies represented remainders of affinity which atoms possess after all their main valencies have been utilised. Compounds formed by the action of main valencies were termed by Werner "compounds of the first order"; whilst when two or more "first order compounds" became united by auxiliary valencies a "second order compound" was produced.

In Werner's view, atoms had no constant valency. The number of atoms which united with a given atom depended upon the nature of the various atoms. There was supposed to be a maximum number of groups which could be retained by auxiliary valencies.

Werner's next assumption was that when a certain number of atoms or groups are attached to a central atom, they filled up the space in the neighbourhood of the central atom; and that therefore there was a maximum possible number of these attached atoms or groups. The space occupied by these groups directly attached to the central atom he called the "first sphere" of the compound. Outside this sphere there might be other atoms, but these were not directly attached to the central atom: Werner imagined them as being attracted to the complex of the "first sphere" as a whole and not as retained by any particular part of it.

The first application of this somewhat complicated hypothesis was made in the field of the cobaltammines. According to Werner, the following model would serve to represent a compound of the type:—

Digitized by Google



The cobalt atom lies at the centre of the molecule. Around it, within the "first sphere" lie the four ammonia molecules and the two chlorine atoms. These six items are "co-ordinated with" the cobalt atom and are so firmly attached that they do not exhibit their usual reactions. Outside the "first sphere" lies the single chlorine atom, which is capable of ionisation; and this atom is not directly connected with any specific atom but is held in position by the attraction of the central nucleus as a whole.

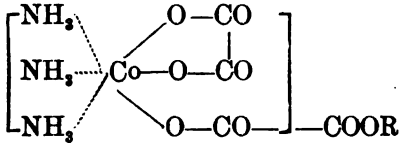
Very little consideration will show that this hypothesis immediately lands us in difficulties when we try to analyse it. In the first place, the compound $CoCl_2$ exists, in which cobalt is divalent; but trivalent cobalt yields no chloride. Assuming cobaltous chloride as a starting-point, it is difficult to see how a fraction of affinity insufficient to retain an extra cobalt atom can yet suffice to hold in combination four whole ammonia molecules as Werner supposed it to do. If his basic hypothesis of the nature of valency be applied here, the two chlorine atoms will rest upon the surface of the cobalt atom and draw upon its store of affinity in proportion to the surface which they overshadow. The entrance of the four ammonia groups, being a subsequent process, cannot displace the cobalt atoms from their rights on the cobalt affinity. Nevertheless, according to the co-ordination hypothesis, the union between the cobalt atom and the two chlorine atoms becomes altered and the chlorine atoms cease to be capable of ionisation. It is quite evident that one or other of Werner's assumptions must be wrong.

Again, as shown in the formula, Werner distinguished, even within the bracket, between the valencies attaching the chlorine atoms and the ammonia molecules; for he represented one set by means of full lines and the other by dotted lines. Apparently he implied that the cobalt was united with the chlorine by a main valency whilst the ammonia molecule was held by an auxiliary one. But if this be so, why should the chlorine atoms not be ionisable, since they seem to be retained

Digitized by Google

by exactly the same kind of affinity as they were originally in cobalt chloride when they had the power of ionisation.

Again, in order to force certain compounds within the bounds of his hypothesis, Werner[1] was driven to resort to formulæ of the following type:—



Here it will be noticed that although both the ends of the oxalic acid chain —O—CO—CO—O— are attached to metallic atoms, cobalt and the metal R, the one end of the chain is "co-ordinated" whilst the other is free to ionise. Whether or not this seems dynamically or chemically possible may be left to the judgment of the reader.

Since the ferrocyanides are among the commonest of complex salts, it is remarkable that Werner's hypothesis completely fails to account for the isomerism in this series. Tetramethyl ferrocyanide, $(CH_3)_4Fe(CN)_6$, is found to exist in two isomeric varieties which are known as the α- and β-forms.[2] The two compounds differ from each other in their solubilities in water and organic solvents; and they behave quite differently in their action with methyl iodide, since the α-form produces a substance, $(CH_3)_6Fe(CN)_6I_2$, which is not obtained from the β-form under identical experimental conditions. Now, in this case, the six cyanogen groups within the bracket are all identical; and there can thus be no isomerism due to them according to the Werner hypothesis since the octahedral grouping must be symmetrical in every respect. None the less, the isomerism appears to be beyond doubt in practice.

Werner's hypothesis was avowedly an attack upon the application of structural formulæ to inorganic compounds in the cobaltammine series; and it is therefore interesting to note that he himself had to take refuge in structural ideas in order to help his hypothesis over a stile. In the case of the compound $Co(NH_3)_5NO_2$, Werner's ideas provided for only one

[1] Werner, *Annalen*, 1914, **406**, 261.
[2] E. G. J. Hartley, *Trans.*, 1913, **103**, 1196.

Digitized by Google

isomer, whereas two isomeric forms are actually known. He evaded this by assuming that the nitrite group could exist in two structural varieties: —O—N : O and —NO_2. Thus he seemed ready to discard structural ideas at one stage and then readopt them later on when driven into a corner.

The complete collapse of Werner's ideas was apparent when he attempted to apply them to simple cases. Misled by some incorrect experimental work of Wedekind,[1] he utilised his "co-ordination" hypothesis to "explain" the existence in two isomeric forms of compounds of the type N . a_2bcd. He showed that his hypothesis demanded that the union of hydrochloric acid with an amine should be represented thus:—

$$NH_3 + HCl = NH_3 \ldots H—Cl$$

the junction between the two molecules being formed by an auxiliary valency. Taking the case of a substituted amine and an alkyl halide, he then declared that different isomers would be formed when (*a*) the amine *abc*N reacted with the halide *a*X; and (*b*) the amine *aab*N reacted with *c*X. In case (*a*) Werner stated that the compound (I.) would be formed; whilst in the case (*b*) the compound (II.) would be produced: and that these would be isomeric according to his hypothesis.

*abc*N . . . *a*X	*aab*N . . . *c*X
(I.)	(II.)

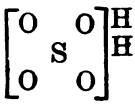
In actual practice, both reactions lead to the same compound; so that evidently Werner's ideas "explain" too much.[2] At a later date he was apparently able to convince himself that the correct result was equally in accordance with his co-ordination ideas,[3] which shows the accommodating manner in which this hypothesis can adapt itself equally well to correct or to erroneous data. Another mare's nest is to be found in the case of the cobalt roseo-salts.[4]

The application of the Werner hypothesis to a familiar compound will suffice to show its weakness. In the case of sulphuric acid, the four oxygen atoms would reside in the "first sphere" of the substance, around the sulphur atom,

[1] See Jones, *Trans.*, 1905, **87**, 1721.
[2] Werner, *Annalen*, 1902, **322**, 261.
[3] Werner, *Neuere Anschauungen* (1909 edition), p. 211.
[4] Werner, *Zeitsch. anorgan. Chem.*, 1897, **15**, 144.

Digitized by Google

whilst the two hydrogen atoms, being ionisable, would be placed outside the sphere :—



But such a formula as this can be sustained only by ignoring the fact that each hydrogen atom is closely associated with an oxygen atom, since the action of phosphorus pentachloride upon sulphuric acid consists in the removal of an oxygen and a hydrogen atom and the replacement of them both by a chlorine atom.

Thus Werner's ideas, though they provide a useful memory-help in the field of the metalammines, do not appear to rest upon very firm foundations ; and it seems probable that their main use in chemistry will eventually turn upon the fact that the true theory of the complex salts—whatever it may be—will arise through some fresh mind destroying Werner's ideas and building something new upon their remains.

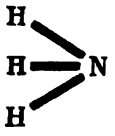
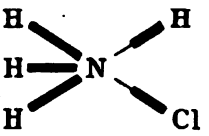
4. *Friend's Views.*

In Friend's view[1] there are three different varieties of valency : (1) free positive valency ; (2) free negative valency ; and (3) residual valency. The first of these is due to an atom's capacity for parting with an electron ; the second is possessed by atoms which can combine with one or more electrons ; so that an element may have both positive and negative valency if it is capable to taking up an electron from one element and parting with it to another. Residual valency (or latent valency) differs from the others in that residual valencies can only be called into action in pairs of equal and opposite sign.

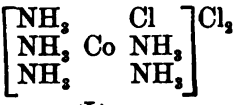
In order to distinguish between free and latent valencies, Friend represents the free type by means of thick lines. For example, in ammonia the three free negative valencies of the nitrogen are saturated. A new negative valency can only be called into play in conjunction with a positive one ; so that ammonium chloride would be represented as shown below :—

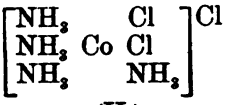
[1] Friend, *Trans.*, 1908, **93**, 260, 1007 ; *The Theory of Valency*, 1908, p. 50.

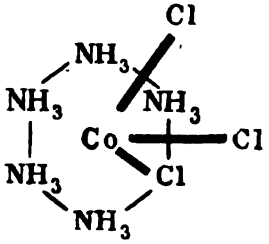
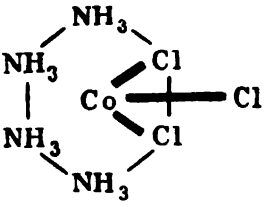
Digitized by Google

Applying this view to the case of complex salts like the cobalt-ammines such as (I.) and (II.), Friend allocates to these the corresponding formulæ shown :—


(I.)


(II.)

Here the chlorine atoms and ammonia molecules form a "shell" around the cobalt atom and are joined together by latent valencies; the ionisable chlorine in (II.) and the two ionisable chlorine atoms in (I.) are joined to the cobalt by free valencies.

The great advantage which this view has over Werner's is that there is no need to assume that a chlorine atom directly attached only to a metallic atom will not ionise in solution.

Suggestions somewhat akin to those of Friend have been put forward by Spiegel,[1] Briggs,[2] and Arrhenius.[3]

5. *The Abegg-Bodländer Hypothesis.*

Abegg and Bodländer[4] advanced a conception of chemical affinity which was further developed by Abegg[5] at a later date. In it, as in Werner's hypothesis, constant valency is not

[1] Spiegel, *Zeitsch. anorgan. Chem.*, 1902, **29**, 365.
[2] Briggs, *Trans.*, 1908, **93**, 1564.
[3] Arrhenius, *Theorien d. Chemie*, 1906, p. 73.
[4] Abegg and Bodländer, *Zeitsch. anorgan. Chem.*, 1899, **20**, 453.
[5] Abegg, *ibid.*, 1904, **39**, 330.

Digitized by Google

supposed to exist, but the valency exhibited by any atom is assumed to depend upon the nature of the atom or atoms with which it unites.*

With regard to the nature of valency itself, Abegg regards all valency as polar in character, even in the case of organic compounds which show no capacity for ionic dissociation. In this direction, his hypothesis is a revival of Berzelius' electrochemical system; and, again following Berzelius, he ascribes a dual electrical character to every atom, so that on this view all the elements are amphoteric in nature.

Novelty enters into the problem at this point, for according to Abegg every element possesses a possible maximum limit to its positive or its negative valency; and the sum of the positive and negative valencies is eight, whilst the total of the positive valencies corresponds to the number of the Group of the Periodic System in which the element is to be found. The action of an element's affinity—whether positive or negative—depends upon the atoms with which it reacts: for example, in its union with hydrogen, iodine utilises its negative valency; whereas when joined to chlorine it exercises its positive valency. When the number of the valency is less than four, Abegg terms the valencies "normal valencies"; whereas when the number exceeds four, he calls them "contra-valencies". The following table gives the relations throughout a short series in the Periodic System:—

	Group I.	Group II.	Group III.	Group IV.	Group V.	Group VI.	Group VII.
Element . . .	Na	Mg	Al	Si	P	S	Cl
Normal valencies .	+ 1	+ 2	3	+ 4	− 3	− 2	− 1
Contra-valencies . .	− 7	− 6	− 5	− 4	+ 5	+ 6	+ 7

Thus chlorine possesses one negative normal valency and seven positive contra-valencies; whilst sodium has one positive normal valency and seven negative contra-valencies. The coming into operation of a normal valency is assumed to extinguish the action of a corresponding contra-valency. On

* The existence of different grades of valency is difficult to account for on this hypothesis. For instance, why should phosphorus yield the two chlorine compounds PCl_3 and PCl_5 and yet not give PCl_4?

Digitized by Google

Abegg's hypothesis, an atom does not necessarily exercise its full valency; and the higher the atomic weight is, the more do the normal valencies diminish in activity and concurrently the contra-valencies become active. Thus in the case of fluorine and iodine, the negative normal valency is strongly active in fluorine but much less so in iodine; whereas the contra-valencies of fluorine show no activity whatever (fluorine forms no oxygen compounds) whilst the whole seven contra-valencies of iodine are active in the case of HIO_4. The influence of the contra-valencies and the difference between the positive and negative types is traced by Abegg in the formation of complex ions, which he supposes to be formed by the addition of a neutral molecule to an ordinary ion by the agency of contra-valencies.

Turning to the question of the union of two or more molecules, Abegg distinguishes between various classes of reaction. According to his views, when the two uniting molecules are identical (association) it is necessary to assume that in the original molecules at least one of the component atoms has not reached its maximal valency; which suggests that one of the elements in the molecule belongs to the higher groups of the Periodic Table. This holds good in the case of molecules like H_2O, NO_2, As_2O_3, SO_3, HF, $AlCl_3$ and $FeCl_3$. Elements of the same type might be expected to be present in compounds which dissociate into two or more molecules in the gaseous condition; and this is supported by the existence of PCl_5, ICl_3 and NH_4Cl. Elements belonging to the higher groups should also be expected to give rise to solid molecular compounds; and this is found to be supported by the occurrence of hydrates, ammoniates, alcoholates and double chlorides such as $PbCl_4,2NH_4Cl$ and $SnCl_4,2SCl_4$.

Abegg has even applied his views to the case of solutions; and he assumed that when the process of solution is accompanied by thermal change or alteration in volume, a molecular compound is being formed. If both solvent and solute have latent valencies, the solvent works against the formation of complexes among the solute molecules which might be produced were the solvent a saturated hydrocarbon like pentane, which he assumed to have no latent valency. In the case of electrolytic dissociation, Abegg postulated the occurrence of three equilibria :—

Digitized by Google

(1) Ion + ion ⇌ undissociated molecules.
(2) Ion + solvent ⇌ compound of ion with solvent.
(3) Undissociated molecules + solvent ⇌ compound of undissociated molecule with solvent.

Feebly dissociating solvents he believed to have no tendency to combine with ions (2). If the tendency to ionisation in (1) is great, the affinity of the undissociated molecules for the solvent in (3) is unimportant, since the non-ionised substance will not reach a concentration comparable with that of the ions.

It must be confessed that Abegg's hypothesis, though interesting, does not assist us much in dealing with definite chemical problems. In the case of complex salts, it is incapable of suggesting to us the probable constitution of the complex ions which might be produced nor does it even throw light upon the number of possible complexes which may be formed. In fact it appears on the whole to be in the nature of an intellectual exercise rather than a helpful instrument.

6. *The Electronic Hypothesis.*

The electronic hypothesis of chemical valency was originated by J. J. Thomson[1] on assumptions which can best be given in his own words. "For each valency bond established between two atoms the transference of one (negatively charged) corpuscle from one atom to another has taken place, the atom receiving the corpuscle acquiring a unit charge of negative electricity, the other, by the loss of a corpuscle acquiring a unit charge of positive. This electrical process may be represented by the producing of a unit tube of electric force between the two atoms, the tube starting from the positive and ending on the negative atom. . . . There is, however, one important difference between the lines representing the bonds and the tubes of electrical force. The lines used by the chemist are not supposed to have direction. . . . On the electrical theory, however, the tubes of force are regarded as having direction starting from the positive and ending on the negative atom."

This conception of valency has been applied to a wide field of chemical problems by Falk and Nelson[2] and at a later date

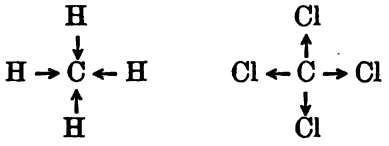
[1] J. J. Thomson, *Corpuscular Theory of Matter*, 1907, p. 138.
[2] For references see p. 291.

Digitized by Google

by Fry.[1] Only a short summary of the results can be given here, which will, however, be sufficient to show the lines upon which the matter has been attacked.

It is at once evident that all the ordinary valency conceptions which are used in structural formulæ can be directly translated into electronic symbols; so that this section of the subject need not be treated at any length. Where the electronic hypothesis promises most is in those cases wherein the ordinary valency ideas have failed to give expression to evidence derived from experiment.

The "direction" factor mentioned by Thomson can be expressed very simply by the use of an arrow instead of the normal line in structural formulæ, the direction of the arrowhead being that in which the electron travels from one atom to the other. Thus methane and carbon tetrachloride are represented in the following manner:—



These formulæ indicate that in methane the carbon atom has gained four electrons which have been transferred from the four hydrogen atoms; whilst in carbon tetrachloride each chlorine atom has acquired an electron from the atom of carbon.

It is reasonable to inquire at this point whether there is any experimental evidence to show that such a transfer of electrons is probable in the hydrocarbons. The only definite proof which could be adduced would be a dissociation of the hydrocarbon molecule into positive and negative ions. This has not been observed in the case of simple hydrocarbons; but the substance $C_{38}H_{30}$ is known to break up in solution into two ions,[2] one of which is supposed to be triphenylmethyl, $(C_6H_5)_3C$.

In the case of hydrazine, the electronic conception offers a satisfactory explanation of a peculiar anomaly. On the

[1] Fry, *The Electronic Conception of Valence*, 1921.

[2] Gomberg and Cone, *Ber.*, 1904, **37**, 2408; Walden, *Zeitsch. physikal. Chem.*, 1908, **43**, 448; a full account of the triphenylmethyl problem is to be found in Stewart's *Recent Advances in Organic Chemistry*, 1920.

Digitized by Google

ordinary structural view, hydrazine is a symmetrical substance, NH_2—NH_2, and since both the amino-groups are alike, it might be supposed that hydrazine would act as a dibasic compound in its union with acids. Actually, however, it is much more akin to a monobasic derivative. On the electronic basis its formula would be written thus—

$$H_2 \rightleftarrows N \rightarrow N \leftrightarrows H_2$$

which is obviously unsymmetrical; so that this formula brings out the difference in reactions exhibited by the two amino-groups. The difference between the dissociation constants of the two carboxyl radicles in a dibasic organic acid might also be accounted for by the dissymmetry of the structure on electronic principles. This dissymmetry can be seen in the case of oxalic acid :—

$$O \leftrightarrows C \rightarrow C \rightleftarrows O$$
$$\downarrow \quad \downarrow$$
$$OH \quad OH$$

Another common example will serve to illustrate a different case. Benzophenone exists in two modifications, one of which melts at 26° whilst the other has a melting-point of 48·5°. Our usual structural formulæ throw no light upon this; but when the electronic formulæ are used, it is found that the two benzophenones can be expressed thus—

$$(C_6H_5)_2C \rightleftarrows O \qquad (C_6H_5)_2C \leftrightarrows O$$
(Stable). (Labile).

These instances are sufficient to show that the electronic hypothesis can account for phenomena which are not representable in our usual structural formulæ; and this certainly marks an advance. At the same time, it must be remembered that if the electronic symbols are pushed to their logical conclusion, they provide for the existence of a large number of compounds of which no trace has been found in practice. For example, a symmetrical tetra-substituted ethylene derivative might be assumed to exist in either of the two forms—

$$R_2C \rightleftarrows CR_2 \qquad R_2C \rightleftarrows CR_2$$

but no more than one variety has been isolated.

Some interesting speculations upon the electronic constitu-

Digitized by Google

tion of complex salts have been put forward by Ramsay,[1] Briggs[2] and De,[3] the latter authors taking the matter up in connection with the atomic volumes of the elements. For further information, however, the reader must consult the original papers, as they can hardly be treated satisfactorily in a brief summary.

The application of electronic ideas of valency to absorption spectra is discussed by McClelland,[4] but here also the original publications must be read.

7. *Conclusion.*

In the foregoing brief survey an attempt has been made to indicate the lines upon which some speculators have worked in the endeavour to solve the problem of chemical affinity; and it must be admitted that no hypothesis has yet been suggested which can be regarded as satisfactory. Either "too much" or "too little" seems to be the main drawback of these modern views; for they appear either to predict cases of isomerism which no research has succeeded in detecting or to leave untouched much that is common ground in chemistry.

The real stumbling-block is, of course, the difference in behaviour shown by organic and inorganic compounds. The development of structural chemistry in the organic field has been so successful, tested as it has been over a range of a hundred thousand compounds and more, that it seems amazing to find the inorganic compounds so refractory when we attempt to bring them within the bounds of the same system. And yet there are great similarities to be detected between, for example, the substitution reactions of benzene and the replacement of one group by another in the complex ions of the cobaltammines.

Inorganic chemistry appears to have attained to a certain stage in the discovery of the Periodic System, but thereafter it made but little progress on the theoretical side. Organic chemistry, on the other hand, has been too much occupied with structural questions, to the exclusion of the problems of reactivity; so that even at the present day we are without

[1] Ramsay, Presidential Address, *Trans.*, 1908, **93**, 774.
[2] Briggs, *ibid.*, 1919, **115**, 278. [3] De, *ibid.*, 1919, **115**, 127.
[4] McClelland, *Phil. Mag.*, 1915, **29**, 192; **30**, 665.

Digitized by Google

symbols which will express the difference in lability between the bromine atom of bromobenzene and that of dinitro-bromobenzene. Whatever view of chemical affinity finally emerges, it is safe to say that it will have to account for both organic and inorganic compounds if it is to be a satisfactory solution of the problem. It is useless to place the two sides of the subject in water-tight compartments, since many of the elements form parts of both organic and inorganic compounds.

Digitized by Google

CHAPTER XVIII.

THE DEVELOPMENT OF THE PERIODIC LAW.

1. *Early Attempts to Classify the Elements.*

WHEN the student is first confronted with the Periodic Table in the pages of some elementary text-book, his not unnatural feeling is one of astonishment that so simple an arrangement was not immediately obvious to chemists at a very early date. Nor is his surprise wholly unjustifiable; for, *taking our present knowledge of the elements for granted*, the discovery of the Periodic Law would not be beyond the power of a clever undergraduate. It is only by examining the history of the subject and noting the difficulties with which the early investigators had to contend that we are able to appreciate their work at its true value and to understand how it was that the Periodic Classification did not come into being at a single stroke but was built up gradually by the labours of different men. In the present chapter a brief sketch of this development will be given, which will be sufficient to show the general trend of these gropings from which the Periodic Law eventually emerged.

It is not necessary to go very far back in the history of chemistry in order to arrive at a date before which the discovery of the Periodic System was practically impossible. Until the atomic theory of Dalton[1] had been accepted, there could be no sound basis upon which to raise a system of the elements. A classification in accordance with chemical properties might have been attempted; but it would have lacked cohesion owing to the difficulty which is experienced in deciding the true chemical nature of an element from a survey of the properties of its compounds. For example, the resemblances between silver and thallium might easily lead to these two elements

[1] Dalton, *A New System of Chemical Philosophy*, 1807-10.

Digitized by Google

being placed in the same class; and the slight solubility of lead sulphate might be argued in favour of an attempt to classify together lead and barium.

Even the coming of the Daltonian theory was not sufficient in itself to make possible the recognition of a periodicity in elemental properties; for periodicity implies a previous arrangement and this arrangement could only come into existence after the determination of atomic weights had been carried out.

Curiously enough, the first attempt to regard the elements as related forms of matter received its incentive not from atomic weight measurements but from Gay-Lussac's law of combining volumes. In 1815, Prout published anonymously,[1] the suggestion that the weights of the atoms of the elements were simple multiples of the weight of a hydrogen atom; and he went the length of conjecturing that hydrogen was the primitive material from which all others were built up. Prout's hypothesis had a considerable influence upon the outlook of certain chemists of whom Marignac was the most important.[2]

It was not until Doebereiner took up the subject, however, that any proper attempt was made to classify elements into groups and to bring out the relations between their atomic weights. He[3] drew attention to the fact that some of the elements could be arranged in groups of three—triads—and that when placed in order of ascending atomic weight the middle element had an atomic weight which was the mean of the two extremes. He also called attention to cases in which the atomic weights of several elements differed but slightly from each other. Among the first type of triads he placed chlorine, bromine and iodine; calcium, strontium and barium; lithium, sodium and potassium: whilst in the second triad group he mentioned platinum, iridium and osmium. Some of his triads, such as lead, silver and mercury, were obviously mistakes due to the difficulty in deciding which atomic weights were correct and which chemical properties were sufficient to qualify elements for inclusion in the same group.

It must be confessed that, although Doebereiner's work

[1] *Annals of Philosophy*, 1815, **6**, 321; 1816, **7**, 113.
[2] Marignac, *Bibliothèque universelle* (Geneva), 1860, **9**, 105.
[3] Doebereiner, *Ann. d. Physik.*, 1829, **15**, 301.

Digitized by Google

marked the first stage in the classification of the elements, its influence was not altogether beneficial. The conception of "triads" appears to have taken strong root in the minds of chemists at this period and later; with the result that in some cases a wider extension of classification was hampered by the determination to seek for "triads" to the exclusion of the more natural grouping of the elements. Pettenkofer,[1] Gladstone[2] and Gmelin[3] appear to have gone outside the triad grouping; but the results obtained by them were very incomplete.

Cooke,[4] in 1854, seems to have departed definitely from the triad idea; and he and Dumas appear to have been the first to suggest a parallelism between the elemental groups and the homologous series of organic chemistry. For example, as the molecular weight increases in the group of the monobasic fatty acids the compounds become less volatile and less reactive, so in the halogens an increase in atomic weight goes hand in hand with diminished volatility and a lessening in chemical activity. Cooke's actual arrangement of the elements in six groups differs considerably from the modern form of the Periodic Table; but, nevertheless, his ideas marked a considerable advance.

Contemporaneously with Cooke, or perhaps rather earlier,[5] Dumas[6] had also drawn a parallel between the homologues of organic chemistry and the grouping of the elements; but his outlook differed in some respects from that of the American chemist, inasmuch as he attempted to bring out certain quantitative relations which he believed to exist among the atomic weights, apart from the mere triad arrangement. Taking the molecular weights of the hydrocarbons, he pointed out that the constant difference of CH_2 between the members of the series gave rise to a system of this type:—

Hydrocarbon.	Molecular Weight.	General Expression.
CH_4	16 = 16	a
C_2H_6	30 = 16 + 14	$a + b$
C_3H_8	44 = 16 + 14 × 2	$a + 2b$
C_4H_{10}	58 = 16 + 14 × 3	$a + 3b$

[1] Pettenkofer, *Annalen*, 1850, **105**, 187.
[2] Gladstone, *Phil. Mag.*, 1858, **5**, 313.
[3] Gmelin, *Handbuch d. Chemie*, Vol. II.
[4] Cooke, *Amer. Jour. Sci.*, 1854, **17**, 387.
[5] See *Brit. Assoc. Report*, 1851.
[6] Dumas, *Compt. rend.*, 1857, **45**, 709; 1858, **46**, 951; **47**, 1026.

Digitized by Google

Now in an analogous manner it is possible to represent the inter-relations of the atomic weights of certain chemically similar elements, as can be seen from the following figures:—

Element.	Atomic Weight.*	General Expression.
Nitrogen . . .	14 = 14	a
Phosphorus . . .	31 = 14 + 17	$a + b$
Arsenic . . .	75 = 14 + 17 + 44	$a + b + c$
Antimony . . .	119 = 14 + 17 + 88	$a + b + 2c$
Bismuth . . .	207 = 14 + 17 + 176	$a + b + 4c$

* The atomic weights are on the hydrogen standard.

From a comparison of the two tables, certain ideas arise. In the first place, both groups of figures show a means of building up the higher weights from the lower by a series of regular increments; though the process is more complex in the atomic than in the molecular table. Secondly, in each case, the lowest homologue displays all the general properties of the series and may be regarded as a "characteristic" or "typical" member, whilst the rest of the group diverge more and more from this type owing to the possession of fresh properties due to the increments. For this reason, in the organic compounds the lowest member of the series stands somewhat apart from the rest; and an analogous gap is traceable between nitrogen and the remainder of the group shown above. If Dumas' ideas were carried to the full, we should be inclined to think that in the elements of Group V. there are three factors present. The first of these, represented by the basic 14, contains all the material which gives rise to the properties of nitrogen. In passing to phosphorus a second factor, represented by the 17, comes into the atomic structure and brings with it the alteration in physical and chemical properties which mark off phosphorus from nitrogen; while at the same time the main properties of nitrogen—tri- and quinque-valency, onium salt formation, etc.—still persist. With the introduction of the third term 44, metallic properties begin to make their appearance in the element, though they are not yet preponderant. But with the increase in the third term to 88 and 176 (thus outweighing entirely the influence of the groups 14 and 17) we arrive at the metallic types of antimony and bismuth. Thus there is much that is suggestive in the ideas of Dumas, though it is not desirable to be carried away by them further than common sense permits.

Digitized by Google

Summarising the foregoing section, it may be said that up to the year 1860 the attempts to classify the elements had not been marked by any great success. Certainly no general scheme had been evolved which satisfied the minds of chemists at the time; and nothing sufficiently logical to impress itself upon the imagination had been produced. Any efforts which had been made were of too patch-work a character to carry conviction.

2. *De Chancourtois and Newlands.*

The task of influencing scientific thought is twofold. In the first place, it is essential to conceive the idea which leads to the opening up of a new field; and secondly, it is necessary to impress that idea upon a world which is often extremely unreceptive of novelties. Thus in estimating the achievements of an investigator, it is desirable to keep these two qualifications in mind and to distinguish clearly between them. If a man discovers a principle, it proves his mental capacity beyond doubt; but if he fails to publish his discovery or if, when published, his work attracts no notice, then his influence upon the development of science may be negligible.

The work which will be described in this section falls within the second class. Both de Chancourtois and Newlands independently discovered the periodicity of properties of the elements when arranged in ascending order of atomic weights; but unfortunately their work failed to catch the attention of chemists and thus its influence upon the progress of chemistry appears to have been nil. None the less it is of historical interest, as proving that the riddle was actually capable of solution at that particular date.

In 1862 and 1863, de Chancourtois[1] handed to the French Academy three papers in which he put forward the thesis that "the properties of the elements are the properties of numbers". His classification took the form of what is known as the Telluric Helix, which he obtained in the following way: The circular base of an upright cylinder is divided into sixteen parts; and a spiral, inclined at 45° to the horizontal, is traced around

[1] A translation of de Chancourtois' first paper is to be found in *Nature*, 1889, **41**, 186; see also *Compt. rend.*, 1891, **112**, 77.

Digitized by Google

the cylinder. Lengths proportional to the atomic weights of the elements are then measured along the spiral; and in this way a series of points is obtained each of which is the "characteristic point" for the corresponding element. When this is done, it is found that elements showing chemical similarities with each other lie in the same vertical line; and when other helices are drawn through two given characteristic points and passing through or near other characteristic points on the surface of the cylinder, it indicates other resemblances between the elements on this "secondary helix". In some cases de Chancourtois' scheme broke down; for example, he grouped magnesium, calcium and strontium together correctly, but iron and uranium also fall on the same vertical line as the other three.[1]

A musical analogy evidently occurred to de Chancourtois, as it was to strike Newlands also, for the French chemist compared his system to that of "a series of musical sounds" and also to "the bands and lines in the spectrum".

Almost simultaneously with de Chancourtois, Newlands[2] approached the same field, though from a different direction. In his first paper, he put forward a classification of elements into eleven groups; and he called attention to the fact that the atomic weights of similar elements often differed from each other by eight or multiples of eight units: but it was not until 1864 that he published an almost complete tabular arrangement. In order to bring this into the shape familiar at the present day it may be printed as below, for in the original the sequence of the elements in order of atomic weight is placed vertically instead of horizontally.

[1] Other spiral arrangements have been described from time to time, but none of them throw any fresh light upon the Periodic Law. See Mendeléef, *J. Russ. Phys. Chem. Soc.*, 1869, **1**, 60; Crookes, *Chem. News*, 1886, **54**, 115; *Trans.*, 1888, **53**, 487; Harkins and Hall, *J. Amer. Chem. Soc.*, 1916, **38**, 169; Soddy, *Chemistry of the Radio-elements*, 1914, II., 9; Stoney, *Phil. Mag.*, 1902, **4**, 411, 504; see also Rayleigh, *Proc. Roy. Soc.*, 1911, **A**, **85**, 471; Carnelley, *Chem. News*, 1886, **53**, 183; Stewart, *Recent Advances in Physical and Inorganic Chemistry*, 3rd edition, 1919, p. 271.

[2] Newlands, *Chem. News*, 1863, **7**, 70; 1864, **10**, 59, 94, 95, 240; 1865, **12**, 83, 94; 1866, **13**, 113, 130; 1872, **25**, 252; 1873, **27**, 318; 1875, **32**, 21; 1878, **37**, 255; see also Newlands, *The Discovery of the Periodic Law*, 1884, which contains all his publications on the subject.

Digitized by Google

NEWLANDS' TABLE OF THE ELEMENTS, 1864 (*Modernised*).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.	IX.	X.	
—	—	—	—	—	—	Li	Li	—	—	
Li	B	C	N	O	F	Na	Mg	—	—	
Mg	—	Si	P	S	Cl	K	Ca	Mo	Pd	Lowest term. / Mean. / Highest term. } Triad.
Zn	—	—	As	Se	Br	Rb	Sr	V	—	
Cd	—	Sn	Sb	Te	I	Cs	Ba	W	Pt	
—	Au	—	Bi	Os	—	Tl	Pb	—	—	

It should be noticed that this table was intentionally incomplete, for Newlands specially added a note to it. "This table is by no means so perfect as it might be; in fact I have some by me of a more complete character, but as the position to be occupied by the various elements is open to considerable controversy, the above only is given as containing little more than those elementary groups the existence of which is almost universally acknowledged."

In his second paper, Newlands advanced his theories a stage further and pointed out that "when the elements are arranged in the order of their equivalents (atomic weights) . . . the eighth element starting from a given one is a kind of repetition of the first, like the eighth note of a octave in music". He also suggested that from his scheme it was possible to predict the existence of elements as yet unknown.

In order to make clear the position of Newlands' work before later investigators entered the field, it may be well to give a modernised arrangement of the grouping of the elements according to the "Law of Octaves" which he published in March, 1866.[1]

NEWLANDS' TABLE OF THE ELEMENTS, 1866 (*Modernised*).

H	Li	Be	B	C	N	O
F	Na	Mg	Al	Si	P	S
Cl	K	Ca	Cr*	Ti	Mn*	Fe*
Co* and Ni*	Cu	Zn	Y	In*	As	Se
Br	Rb	Sr	Ce and La	Zr	Di* and Mo*	Rh* and Ru*
Pd*	Ag	Cd	U*	Sn	Sb	Te
I	Cs	Ba and V*	Ta*	W*	Nb	Au*
Pt* and Ir*	Os*	Hg	Tl	Pb	Bi	Th*

In the above table, the asterisks mark those elements which are wrongly placed according to modern views; and it will be

[1] See *Chem. News*, 1866, **13**, 113.

Digitized by Google

seen that out of a total of sixty-three elements, Newlands had succeeded in classifying correctly no less than forty-four—by no means a discreditable result, especially in view of the knowledge at his disposal at the time when he worked. His failures are ascribable to three causes. In the first place, he evidently adhered much too closely to his idea of Octaves, with the result that he missed the significance of what we now term the Eighth Group. Next, owing to scandium being unknown at that date, the sequence of elements in the third line of his table is not the natural one. Thirdly, several of the atomic weights which he used were erroneous, the true atomic weight not being known until later.

To the foregoing table, objections were made on the ground that it left no possibility for the insertion of any further elements which might be discovered. To this Newlands[1] replied that his table was intended to bring out the existence of a simple relation among the elements when arranged in order of their atomic weights; and that the discovery of new elements in the future would not necessarily disprove this relationship though it might modify the form of the table.

Newlands' own claims[2] to priority in the matter of the classification may be given here, since they exhibit clearly the advances which he had made; and they are worth comparing with the later work of Mendeléef. Newlands was the first to publish the principle of the Periodic Table as we have it to-day. He applied his Law of Octaves to (1) the prediction of new elements, as shown by gaps in his tables; (2) the prediction in 1864 of the atomic weight of germanium, which element was not discovered until 1886; (3) the prediction of the atomic weight of indium which had not been experimentally established; (4) the selection out of two possible numbers of the correct atomic weight for beryllium; (5) the grouping of certain elements according to the Law instead of according to the system in vogue; (6) the relation of the Law to physical properties, showing that similar terms from different groups, such as oxygen and nitrogen or sulphur and phosphorus, frequently bear more physical resemblance to one another than they do to the remaining members of the same chemical group.

[1] Newlands, *Chem. News*, 1866, 13, 130.

[2] Newlands, *The Discovery of the Periodic Law*, 1884, p. vii.

Digitized by Google

With this series of easily verified successes to his credit, one cannot help asking how it came about that Newlands was not immediately hailed as a great discoverer and why it was left to later workers to reap the credit which he evidently deserved. Various factors seems to have contributed to defeat his efforts. In those days, the knowledge of atomic weights was still uncertain in many cases; and the chemical public was more interested in the results of new determinations than in attempts to co-ordinate the figures already obtained. Even an accepted basis for atomic weights was lacking. In the first half of the nineteenth century, a struggle had been going on between two systems advocated respectively by Berzelius and by Dumas; and when, after the breakdown of Berzelius' system, Dumas' views seemed to be coming to their own, they were supplanted in turn by Gmelin's proposals. The year 1842 saw the birth of yet another system, put forward by Gerhardt, which gained in popularity and displaced Gmelin's method of representation. Thus at the middle of the century, the whole field of atomic weights was confused by the co-existence of new and old standards; and several systems were in vogue which were mutually incompatible. In 1860, Cannizzaro carried the chemical world with him in his definition of atomic weight; and it is a proof of Newlands' sagacity that he selected the Cannizzaro system when he set out to trace a relationship between the atomic weights. When this state of confusion of standards is borne in mind, it is clear that the claims of elemental classifications could hardly be considered with much eagerness. The period, indeed was one in which "facts and not theories" might well be the cry of the chemist.

But in addition to this state of affairs, other influences confronted Newlands. It is reported[1] that when the Law of Octaves was propounded at a meeting of the Chemical Society, "Professor G. Foster humorously inquired of Mr. Newlands whether he had ever examined the elements according to the order of their initial letters". It is not often that humour makes a permanent reputation for a scientific worker; but Professor Foster's attitude when confronted for the first time with the Periodic Law does not lack a certain

[1] See *Chem. News*, 1866, **13**, 113.

Digitized by Google

comic element which perhaps he himself may have appreciated in later years.

3. *Mendeléef.*

Newlands had failed to win recognition for his system of classification; but almost immediately there appeared on the scene two personalities, more forcible or more fortunate, which between them were to succeed in compelling the chemical world to take note of new views. The question of priority of ideas is a somewhat unfruitful one; but in this case it may be said that there is evidence* that Lothar Meyer was rather ahead of Mendeléef in conceiving the Periodic System; but that his actual publication was the later of the two.[1] In the present section, it will be most convenient to deal with Mendeléef's work, since it follows naturally upon that of Newlands, although Newlands' investigations appear to have been unknown to his successor.

The form of the table published by Mendeléef[2] in March, 1869, is given in the modernised form below, so that it may be compared with the earlier work of Newlands.

MENDELÉEF'S TABLE OF ELEMENTS, MARCH, 1869 (*Modernised*).

					H*								Li				
						Be	B	C	N	O	F	Na					
						Mg	Al	Si	P	S	Cl	K	Ca	?	Er*	? Yt*	? In* ?
					Ni												
Ti	V	Cr	Mn	Fe	Co	Cu	Zn	?	?	As	Se	Br	Rb	Sr	Ce*	La*	Di*	Th*
Zr	Nb	Mo	Rh*	Ru*	Pd	Ag	Cd	U*	Sn	Sb	Te	? I	Cs	Ba				
?	Ta	W	Pt*	Ir*	Os*	Hg*	—	Au*	—	Bi	—	—	Tl	Pb*				

Here, as in Newlands' table on p. 317, the elements which do not occupy the positions accepted at the present day are marked with asterisks. It will be seen that both Newlands and Mendeléef classified sixty-three elements. Of these, Newlands placed forty-four correctly, whilst Mendeléef was

[1] Mendeléef, *J. Russ. Phys. Chem. Soc.*, 1869, **1**, 71, 229; *Zeitsch. f. Chemie*, 1869, p. 405; L. Meyer, *Annalen* (*Suppl.*), 1870, **7**, 358.

[2] See *Zeitsch. f. Chemie*, 1869, p. 405.

* See Bedson, Lothar Meyer Memorial Lecture, *Trans.*, 1896, **69**, 1403. A draft of the Periodic Table was drawn up by Meyer in 1860; and a copy of the completed form was handed by him to a friend in July, 1868. Mendeléef's first paper appeared in the early part of 1869. Compare L. Meyer, *Ber.*, 1880, **13**, 259, 2043; Mendeléef, *ibid.*, 1796.

Digitized by Google

correct in forty-six cases; so that the difference between the two workers was not great at this period.

This table of 1869, it will be noted, does not contain the usual main and sub-group arrangement which is now common in text-books. It was not until August, 1871, that Mendeléef adopted this form, as shown below :—

MENDELÉEF'S TABLE OF THE ELEMENTS, 1871 (*Modernised*).

I.	II.	III.	IV.	V.	VI.	VII.	VIII.
H							
Li	Be	B	C	N	O	F	
Na	Mg	Al	Si	P	S	Cl	
K	Ca	—	Ti	V	Cr	Mn	Fe Co
(Cu)	Zn	—	—	As	Se	Br	Ni Cu
Rb	Sr	Yt	Zr	Nb	Mo	—	Ru Rh
(Ag)	Cd	In	Sn	Sb	Te	I	Pd Ag
Cs	Ba	Di	Ce	—	—	—	
(—)	—	—	—	—	—	—	
—	—	Er	La	Ta	W	—	Os Ir
(Au)	Hg	Tl	Pb	Bi	—	—	Pt Au
—	—	—	Th	—	U	—	

It is not without interest to compare Mendeléef's claims with those of Newlands. In his Faraday Lecture,[1] Mendeléef summarised as follows the essence of the Periodic Law: (1) When arranged according to their atomic weights, the elements exhibit a periodicity of properties; (2) Elements which are similar in properties have atomic weights which are either of almost the same value (*e.g.*, in the platinum group) or increase regularly (*e.g.*, the alkali metals); (3) The arrangement of the elements corresponds to their valencies; (4) The discovery of some unknown elements may be expected; (5) The atomic weights of the elements may be amended in some cases; (6) The elements which are widely diffused in nature have small atomic weights; (7) The magnitude of the atomic weight determines the character of an element; (8) Certain characteristic properties of an element may be foretold from its atomic weight.

When the first five of these statements are compared with the six claims of Newlands, quoted on p. 318, it will be found that the two sets are practically identical. All that Mendeléef

[1] Mendeléef, *Trans.*, 1889, **55**, 634.

Digitized by Google

ascribed to the Periodic Law had already been achieved by the Law of Octaves. As to the seventh and eighth clauses, they appear to be complements of each other; and neither of them was correct even in Mendeléef's day as far as the rare earth elements were concerned. Finally, the sixth clause has nothing to do with the Periodic Law; it could have been arrived at even had the periodicity of chemical properties never been discovered.

On the face of things, then, Mendeléef had achieved nothing which Newlands had not already brought before the chemical world; and it is reasonable to speculate upon the success of the one investigator and the comparative failure of the other in the attempt to draw attention to the periodicity in elemental properties. Why did Mendeléef succeed where Newlands failed?

In the first place, the atmosphere had changed. The year 1860 had seen a congress of a hundred leading chemists at Karlsruhe, the object of which was to adopt a final standard of atomic weights; and although during the congress itself there was much dissension, the arguments of Cannizzaro had eventually carried the day and the modern system of expression had become more generally supported by the time Mendeléef published his papers than it was when Newlands attempted to gain recognition. This in itself was a powerful factor in the fortunes of the Periodic Arrangement.

Again, the characters of the two men, as far as can be judged from their writings, were very different. Newlands showed a certain caution in his exposition, trying, apparently, to play his strong cards while retaining his weak ones in his hand. This attitude is visible in the quotation given on p. 317, in which he evidently feared to bring out his complete system lest it should be attacked on some weak point. Mendeléef, on the other hand, had no such hesitations. His statement of the Periodic Law was dogmatic and written throughout with the air of confidence. Where Newlands made tentative suggestions, Mendeléef asserted his views bluntly, almost without qualification. Not only so, but while Newlands' predictions took the form of the statement that a certain element might subsequently be discovered, Mendeléef had the courage to calculate the exact properties

Digitized by Google

Digitized by Google

UNIV. OF CALIFORNIA

SYSTEM.

IV.	GROUP V.
C 6	N 7
Si* 14	P 15
	V 23
Ge 32	As 33
	Cb 41
Sn 50	Sb 51
— Sm 61 62	
u Ct 1 72	Ta 73
) and topes[2] 82	Bi and 4 isotopes[3] 83
	EkaTa UX_2 91

Th-D, Ac-D and Ra-F.

the Atomic Numbers of the
ass spectrum analysis to be

Digitized by Google

which the new element and its compounds would exhibit. This attitude of certainty had, doubtless, a "moral effect" upon the minds of those who studied his papers.

Reference to a modern form of the Periodic Table given opposite will serve to bring out the following points upon which Mendeléef laid stress. The elements are arranged in eight vertical columns which are termed groups, and in twelve horizontal lines which are designated as Series. Each group contains two sets of elements which have a general resemblance, though the members of each sub-group have more kinship with each other than with the elements of the other sub-group. Elements of the odd Series are, in general, much more easy to obtain in the free state than are the elements belonging to the even Series. The members of the odd Series readily form alkyl derivatives, whilst even Series elements rarely have this property. In nature, it appears to be a rough rule that members of the even Series occur as oxides or oxide derivatives, whereas the odd Series elements often occur naturally in the form of sulphides. The oxides of the even Series elements are as a whole much more basic in character than the corresponding compounds of the odd Series. Curiously enough, the elements from lithium to silicon, inclusive, appear to stand outside the general rules with regard to odd and even Series.

Mendeléef's Table, even in its most perfect form, is by no means free from defects. Some of these will be dealt with on a subsequent page; and, for the present, attention may be confined to the two extreme Groups, I. and VIII. One of Mendeléef's claims as put forward above, was that his arrangement brought the elements into a regular order as regards valency; and in general this claim was justified. None the less, the classification of copper, silver and gold together along with the alkali metals certainly does not support Mendeléef's thesis; for although all three metals can act as monovalent elements, copper also gives divalent derivatives and gold is a trivalent element. There is, therefore, just as much reason for placing arsenic along with the Group III. elements as there is for classifying together gold and sodium.

Again, Mendeléef in general took the hydrogen and oxygen

Digitized by Google

compounds of the elements as guides to their valency. On the hydrogen basis boron might belong to Group IV., for its hydrogen derivative has the formula B_2H_6 (which is an exact parallel to C_2H_6).

Finally, the elements of Group VIII. ought to be octavalent if the valency rises steadily from left to right through the groups; but in actual practice rhodium and osmium appear to be the only two members of the group which are capable of octavalency in their oxides, the others being either hexavalent or of even lower valency grades.

4. *Lothar Meyer.*

With a certain jealousy, Mendeléef appears to have wished to decry the originality of Lothar Meyer's contributions to the classification of the elements; and in his Faraday lecture[1] the only mention which he made of his competitor was the grudging statement that "In the following year" (after Mendeléef's first publication) "Professor Lothar Meyer, in his well-known paper, studied the same subject in more detail and thus contributed to spread information about the Periodic Law". From this statement it would hardly be possible to deduce the value of Lothar Meyer's work or the fact that he brought into view a series of periodic relations which Mendeléef himself had almost entirely missed.*

Like Mendeléef, Lothar Meyer[2] published a tabular arrangement of the elements; but here, as we have seen, he had many predecessors. His freshness of outlook was exhibited in the discovery of a periodicity which exists in the atomic volumes and other physical properties of the elements. Proceeding upon the assumption that atoms are aggregates formed from one type of matter and differing only in their masses, Lothar Meyer selected the volumes of the atoms as criteria for the change in properties which is observed as we pass from element to element. Dividing the atomic weight of the

[1] Mendeléef, *Trans.*, 1889, **55**, 634.

[2] L. Meyer, *Annalen* (*Suppl.*), 1870, **7**, 358; see also his *Modern Theories of Chemistry*.

* Mendeléef (*J. Russ. Phys. Chem. Soc.*, 1869, **1**, 229) mentioned that "the comparison of the densities and volumes of the elements in certain Series furnishes proof of the 'naturalness' of the system" of classification. It is evident that he failed to appreciate further possibilities.

Digitized by Google

elements by their respective densities in the solid state, Meyer obtained the "atomic volumes"; and by plotting these figures as ordinates whilst the weights of the atoms were represented by abscissæ, he was able to show that there was a periodic systole and diastole in the volume as the atomic weight was increased. The graph at the end of this volume shows the type of curve thus produced.* A glance at this curve of atomic volumes will be sufficient to show the number of parallel relationships which it brings out. Melting-points of the elements rise and fall periodically; refractivity is a periodic property; the electrochemical character of the elements undergoes regular alterations along the series; brittleness and malleability alternate with a fair regularity; and even the colours of chlorides show a certain periodicity. The mere inspection of the graph displays a marvellous connection between various elemental properties such as was only dimly appreciated when the tabular arrangement of the elements was employed.

The relationships exhibited by Lothar Meyer's curve are almost self-evident; but it seems not without interest to draw attention to the light which it throws upon the arrangement of the Periodic Table. Examination of the curve shows that it consists of five complete waves and the fragments of a sixth and a seventh. The five complete waves have their troughs at carbon, aluminium, nickel, ruthenium and osmium; the incomplete first wave begins at hydrogen and the fragment of the final wave ends at uranium on the way to another trough. There is nothing in the form of the curve which suggests anything like the A and B sub-groups in Mendeléef's Table; for in the curve each element in the wave seems to follow naturally upon its predecessor. It might be said, however, that the series K, Ca, Sc, Ti represents a steady decrease in the atomic volume whilst the corresponding sub-group Cu, Zn, Ga, Ge is marked by a regular increase in the same property.

It is, of course, well known that similar elements occur at corresponding points on the curve: thus all the alkali metals are placed at the crests (if lithium be excepted); all the halogens lie on the right-hand side of the wave; and the elements

* In this curve the abscissæ are atomic numbers and not atomic weights; but the type of curve is much the same.

Digitized by Google

of the transitional type like carbon, silicon, iron, palladium and platinum are situated at the troughs of the various waves.

Thus by devising the curve of atomic volumes, Lothar Meyer was able to bring clearly into prominence not only the chemical but also the physical properties of the various elements and to group their inter-relationships into a form which is rapidly appreciated by the eye. In this divergence from the beaten track of classification he seems to have surpassed Mendeléef by a stride much longer than the advance which Mendeléef could claim to have made upon Newlands. Mendeléef devised something very like the modern Periodic Table; in doing so he was proceeding upon the same lines as previous investigators: but the originality of Lothar Meyer places him in a different class.

Curiously enough, Mendeléef at the time reaped the main credit. Lothar Meyer in his exposition of his discoveries [1] tended rather to the side of scientific caution. His attitude towards his own work was that of a critic rather than of an advocate; and it is possible that this modesty of tone led to his being ranked on a lower level than the more self-assertive Russian.

5. *The Fulfilment of Mendeléef's Predictions.*

It was one of Mendeléef's guiding ideas that the discovery of natural laws is not the ultimate object of scientific research. In his view, unless the formulation of a new law opened up a fresh field for further investigation, the law had little interest in itself. With this in his mind, he had not hesitated to show how the Periodic Law might be utilised as an incentive to further work.

In his early publications he drew attention to the fact that the current atomic weights of some elements such as uranium and indium could not be brought into agreement with his classification; and he suggested that further research upon these subjects would lead to different results. In 1869, uranium was supposed to have an atomic weight of 120 and indium was known to have an equivalent of 37·7, which left 37·7, 75·4,

[1] See his *Modern Theories of Chemistry*, 1888. This work may be strongly recommended even at the present day owing to the breadth of its treatment and the interest of the speculations contained in it.

Digitized by Google

113·1 or higher atomic weights possible. According to Mendeléef, uranium's atomic weight must be somewhere near 240, and the position of indium should be between cadmium and tin, which would give it an atomic weight of about 114. These predictions and several others of the same type were justified by later and more accurate determinations of the atomic weights concerned; and thus the value of the Periodic Law was demonstrated in the clearest manner.

The most striking success, however, was obtained in the case of the three elements scandium, gallium and germanium. None of these three metals was known in 1871, nor was there any reason to suspect their existence, apart from the occurrence of gaps in the Periodic Table; yet Mendeléef did not hesitate to predict not only their existence but even the numerical values of their principal constants. The discovery of the three metals (scandium, 1879; gallium, 1876; and germanium, 1886) proved that Mendeléef's prophecies were accurate to an almost uncanny degree, as can be seen from the following table:—

Mendeléef's prediction[1] of the properties of "Eka-silicon" in 1871.	Properties of Germanium, discovered in 1886.
Dark grey lustrous metal.	Greyish-white lustrous metal.
Very hard to fuse.	M.P. 900° C.
Atomic weight about 72.	Atomic weight 71·93 on hydrogen standard.
Density about 5·5.	Density = 5·469.
Atomic volume = 13.	Atomic volume = 13·2.
Specific heat = 0·073.	Specific heat = 0·076.
Oxide EsO_2 of density = 4·7 and molecular volume = 22.	Oxide GeO_2 of density = 4·703 and molecular volume = 22·16.
Chloride $EsCl_4$, liquid, B.P. about 90° C., density = 1·9.	Chloride $GeCl_4$, liquid, B.P. = 86° C., density = 1·887.
Ethyl derivative $Es(C_2H_5)_4$, B.P. = 160° C., density = 0·96.	Ethyl derivative $Ge(C_2H_5)_4$, B.P. = 160° C., density = about 1·0.

The discovery of these three elements and the verification of Mendeléef's predictions as to their properties served to establish the Periodic Law upon the firmest possible foundation. Not even the discovery of the planet Neptune can be classed in the same category as this work of Mendeléef; for the calculations of Adams and Leverrier were based upon the definitely measured perturbations of Uranus, that is, upon something which implied the existence of a cause, whereas the Russian

[1] Mendeléef, *J. Russ. Phys. Chem. Soc.*, 1871, 3, 25.

Digitized by Google

chemist had nothing but faith in the accuracy of his classification to plead in support of his forecasts.

In view of the success of Mendeléef's other prophecies, it may not be amiss to recall here one[1] which seems to have dropped out of public notice. In the series which contains mercury, lead and bismuth, Mendeléef predicted the existence of an element which he called dvi-tellurium. It should be an analogue of tellurium with an atomic weight of 212 and an oxide DtO_3. In the free state it should be an easily fusible, non-volatile metal, crystalline and of a grey colour, with a density of about 9·3. It should form a second oxide DtO_2, endowed with feeble acidic and basic properties On active oxidation, DtO_2 should give the higher unstable oxide DtO_3, which should resemble PbO_2 and Bi_2O_5 in properties. Dvi-tellurium hydride, if found to exist, should be less stable than H_2Te. The compounds of dvi-tellurium should be easily reduced; and the metal itself should form alloys with other metals. This prediction evidently refers to what we now know as polonium; and it will be of interest to learn the properties of polonium when they have been more fully examined.

6. *Other Confirmations of the Periodic Arrangement.*

Once the Periodic System had gained recognition, it was natural that its influence should stimulate research in all branches of inorganic chemistry. Atomic weights which did not concord with the scheme had to be checked and corrected; the chemical properties of certain elements had to be studied afresh in order to see whether further work upon them would support or destroy Mendeléef's views; and a score of other problems had to be taken in hand which would probably have remained dormant had not Lothar Meyer and Mendeléef succeeded in impressing their ideas upon the minds of chemists.

Of the workers in this field, the most untiring was Carnelley;[2] but space will not permit the description of his researches. By the collection of an immense quantity of data, he was able to show that periodicity was not merely a function

[1] Mendeléef, Faraday Lecture, *Trans.*, 1889, **55**, 649.

[2] A summary of Carnelley's work together with full references is to be found in *Chem. News*, 1886, **53**, 157, 169, 183, 197.

Digitized by Google

of the elemental series but that it extended equally to the compounds of the elements. He examined, *inter alia*, melting-points, boiling-points, heats of formation and specific gravities. In addition to these, periodicity has been traced in other properties such as refractivity, hardness, compressibility, thermal coefficients of expansion, and the coefficients of thermal and electrical conduction.

Thus the periodic variations in the properties of the elements themselves are accompanied by analogous periodicities which can be traced even through a series of compounds; and the Periodic System has gained immensely in strength by this enlargement of its scope.

7. *Crookes.*

Very little thought will show that in all the systems hitherto described in this chapter there has been one underlying assumption. The atoms of two different elements were supposed to be dissimilar in character; but all the atoms of a single element were tacitly assumed to be identical in all their properties. Every chlorine atom was believed to have exactly the same characteristics as any other chlorine atom; and the classification of the elements implied the separation of matter as a whole into various categories in each of which the material was homogeneous.

It was not until twenty years after the modern Periodic System had taken root that Crookes[1] suggested a fresh outlook. Possibly, he suggested, this assumption of elemental homogeneity was unjustified; and, when the elements themselves were examined more closely, the atoms of which they were composed might not all be found absolutely identical in character. In the actual course of events it has been shown that Crookes was wrong in the particular case to which he applied these views—the elements of the rare earth group—but the ideas which he put forward have been proved to be correct on a scale much more extensive than could have been anticipated. He did not hesitate to predict that an "absence of absolute homogeneity may possibly yet be traced in many of the 'elements' if once the right reagents are selected";

[1] Crookes, Presidential Address, *Trans.*, 1888, **53**, 487.

Digitized by Google

and this prediction has now been verified by the application of mass-spectroscopy methods.

In order to make his views clear, Crookes employed a crude analogy which may be quoted here. "If we take any very frequented street in London, say Fleet Street, at a time when the animated current runs pretty equally in two directions, and if our speed of walking is somewhat greater than the mean speed of the other foot passengers, we shall observe that the throngs on the footways are not evenly distributed, but consist of knots or groups—we might almost say blocks—with comparatively open intervening spaces. The explanation of this unequal agglomeration of individuals is simple. Some two or three persons whose rate of walking is slower than the average somewhat retard the movements of other persons, whether travelling in the same or in the opposite direction In this way a slight temporary obstruction is created. The persons behind catch up to the obstruction, and so increase it, while those in front of the obstruction, hurrying on unhindered at their former rate, leave a comparatively free and open space, until they, too, find themselves delayed further on by another little group of loiterers."

Crookes pointed out that this process of segregation was common to all types of particles moving with different speeds; and that a similar gathering into groups could be detected when mixtures of powders of different densities were shaken with water in horizontal tubes. He attributed to analogous causes the striations which are observed in the discharge of electricity through gases under moderate pressures.

Proceeding from this analogy to the case of the elements, he continued: "In the molecule of a certain group let the form of energy which has for a factor what we call atomic weight be represented by the figure 35·5; it follows, from the foregoing exposition—which I have endeavoured to make clear —that whilst the great bulk of its component atoms have this atomic weight, a small percentage may vary from this figure to the extent of a decimal place, while a few others may stray as much as a whole number or two on one side or the other of the mean. The ultimate atoms whose rates are not exactly 35·5, but a little higher or lower than 35·5, will congregate around the 35·5 nucleus, forming a group whose average value

Digitized by Google

will be 35·5. In like manner, similar groups will be formed having the average rates of 80 and 127, whilst intermediate spaces will be cleared, the ultimate atoms which occupied these lone spaces being attracted to the chlorine, bromine and iodine groupings. These groupings represent what at present we call elements, but which I conjecture may possibly consist each of an element and of a certain group of meta-elements, or each may be formed of a whole group of meta-elements, none of which greatly preponderates over the remainder.

From this quotation, it is evident that Crookes believed that the atoms of a single "element" might differ from each other by quantities greater than a single unit of atomic weight; and as will be seen later in this chapter, his views in this field have been triumphantly vindicated.

It is rather depressing to find that at the time, and even in the first decade of the twentieth century, many chemists regarded Crookes' views as pure fantasy. Thus again in the history of the Periodic System the exposition of the truth failed to convince a scientific audience.

The objection might be brought against Crookes' ideas that in the course of time, his hypothetical "meta-elements" would become sifted out from the main mass of the "element" around which they had accreted; but it must be remembered that Crookes postulated an almost complete identity in *chemical* character between the various atoms. As can be seen above, he did not regard the chemical characters of his various forms of an "element" as being absolutely identical; but from his general exposition it is clear that he believed that none of the ordinary reactions with which we are familiar would suffice to separate one type of atom from another.

In the view of Mendeléef[1] the Periodic System implied the existence of a limited and definite number of elements in each period; and it seemed as though the conception of the meta-elements conflicted with this idea. According to Crookes, however, if the Periodic Table could not provide for the meta-elements, then the fundamental basis of the Periodic Law must be modified.[2] "But if we suppose the elements reinforced by a vast number of bodies slightly differing from each other in

[1] Mendeléef, *Principles of Chemistry*, II., pp. 19 ff.
[2] Crookes, Presidential Address, *Trans.*, 1888, 53, 490.

Digitized by Google

their properties, and forming, if I may use the expression, aggregations of nebulæ where we formerly saw, or believed we saw, separate stars, the periodic arrangement can no longer be definitely grasped. No longer, that is, if we retain our usual conception of an element. Let us then modify this conception. For 'element' read 'elementary group,' such elementary groups taking the place of the old elements in the periodic scheme—and the difficulty falls away. In defining an element, let us not take an external boundary, but an internal type. Let us say, *e.g.*, that the smallest ponderable quantity of yttrium is an assemblage of ultimate atoms almost infinitely more like each other than they are to the atoms of any approximating element. It does not follow that the atoms shall all be absolutely alike among themselves. The atomic weight which we ascribe to yttrium, therefore, merely represents a mean value around which the actual weights of the individual atoms of the 'element' range within certain limits. But if my conjecture is tenable, could we separate atom from atom, we should find them varying within narrow limits on each side of the mean."

Looking back upon this Address of Crookes', it is impossible not to be impressed by the perspicacity which he displayed. More than a quarter of a century was to pass before his far-reaching views were justified by the test of experiment; but our ideas of the Periodic Table to-day are those of Crookes and not those of Mendeléef. We now know that the various places in the Table are not occupied by homogeneous systems but that in many cases the "elements" are mixtures of more than one kind of atom.

8. *The Zero Group.*

An examination of Mendeléef's Table of 1871 (see p. 321) will reveal one peculiarity. Beginning with the strongly electropositive element lithium, the series contains elements of increasing valency and diminishing basicity—beryllium, boron, carbon, etc.—until it ends sharply with the electronegative fluorine. The next element is sodium, which is strongly electropositive. Here, then, there is an abrupt transition from electronegative to electropositive character, with no intermediate link. On the other hand, when a start is made at potassium,

Digitized by Google

it is found that the acidic type of element in the series is not so marked in its character; and that with manganese (which corresponds to the halogens in the Table) there is nothing to parallel the extreme electronegative character of fluorine. In fact the series at this point shows a gradual transition in character, passing from acidic chromium through manganese to the Eighth Group and then on to copper and zinc without the interposition of any markedly negative element having appeared. Thus against the abrupt transition which occurs in the series O, F, Na, Mg we can only set the gradual change in properties of the group Cr, Mn, Fe, Co, Ni, Cu, Zn. By analogy, there should lie between fluorine and sodium some element which will form a transition, just as the Group VIII. elements furnish an intermediate stage between manganese and copper. The order of the atomic weights suggests something of the same kind; for there is a gap of four units between fluorine and sodium, whereas the usual difference between two successive elements is about two units.

It is curious that Mendeléef's acute mind did not appreciate the meaning of this phenomenon; but no one appears to have grasped the possibilities in this instance. The discovery of the intermediate elements came as a complete surprise to the chemical world when in 1894 Rayleigh and Ramsay isolated argon, the first of the group. Not only so, but even after the discovery there seems to have been considerable difficulty in finding a place for this new element in the Periodic System, a difficulty which was increased by the fact that the atomic weight of argon did not lie between those of chlorine and potassium, but was rather higher than that of the metal.

Thomsen[1] appears to have been the first to see the full bearing of the new advance. He predicted that argon was the representative of no less than six new gaseous elements which would lie between the halogens and the alkali metals and which would have atomic weights approximating to 4, 20, 36, 84, 132 and 212. His forecast is not absolutely correct, since the actual weights are: helium, 4; neon, 20·2; argon, 39·9; krypton, 82·92; xenon, 130·22; and niton, 222; but considering the state of knowledge at the time, Thomsen's prophecy almost deserves to rank with those earlier ones made by

[1] Thomsen, *Zeitsch. anorgan. Chem.*, 1895, **9**, 283

Digitized by Google

Mendeléef. Thomsen further pointed out that the inert gases formed the transitional group between the halogens and the alkalis; and that the abrupt change in electrochemical character was bridged by the properties of the new elements:—

Fluorine	Neon	Sodium
Electronegative.	Zero.	Electropositive.

Thus by the work of Ramsay and Rayleigh, a new group was added to the Periodic Table, which rounded off the classification in a satisfactory manner and left no ragged edges.

The introduction of the Zero Group led Mendeléef to put forward a further speculation. If a Zero Group was required to complete the horizontal part of the Table, it is possible to suppose that there should be a corresponding addition to the Series as well; and that above the series beginning with helium, two new series should be introduced, one of which would be a Zero Series, thus:—

	Group 0.	Group 1.
Series 0 . . .	x	—
Series 1 . . .	y	H
Series 2 . . .	He	Li

Mendeléef [1] assumed the existence of at least two new elements, designated x and y, one of which he suggested might be the element coronium with an atomic weight of 0·4, whilst the other, with a maximum atomic weight of 0·17, he believed might be the luminiferous ether.

9. *Isotopes and Isobares.*

In the foregoing pages, the slow evolution of the Periodic Table has been traced step by step from the fragmentary triad system up to the culmination in the discovery of the gases of the Zero Group; and it may be recalled that throughout that long process of development the atomic weights of the elements formed the basis upon which the classification reposed. Here and there, in the case of iodine and tellurium or of cobalt and nickel, the sequence of atomic weights was not exactly that of

[1] Mendeléef, *Principles of Chemistry*, 1905.

Digitized by Google

the chemical properties; but these examples were regarded as chance anomalies which did not affect the validity of the main system; and little attention was paid to them except in the hope of bringing the inverted pairs into line with the rest of the categories by a revision of the atomic weights.

In 1910, evidence had come to light which was to bring collapse to the whole atomic weight basis of the Periodic System. Soddy[1] pointed out that certain members of the radioactive group of elements exhibited complete identity of chemical behaviour: thorium, ionium, radiothorium and radioactinium are chemically indistinguishable from each other; thorium-X, actinium-X and radium are chemically inseparable. Yet each of these materials has a definite radioactive character which distinguishes it from the other members of the same class; and therefore the atoms of, say, ionium and thorium cannot be identical in every respect.

Following out this line of thought in the following year, Soddy[2] put forward the view that chemical analysis, instead of being a process of separating matter into various grades such that every particle in the one grade is identical with its neighbours, is merely a method of gathering matter into a series of "types" which are internally homogeneous only as far as chemical character is concerned. Each "type" is easily separable by chemical methods from matter belonging to another "type"; but the matter included in the single "type" may be heterogeneous in reality, although homogeneous as far as chemical reactions go. Thus two atoms may be identical in chemical behaviour but may differ from each other in atomic weight or in radioactive character.

To express this idea, Soddy coined the word *isotopes*. When two or more elements are chemically inseparable and yet are distinguishable by non-chemical differences, such as differences in radioactivity or differences in atomic mass, they are said to be a group of isotopes; and within the group the members are described as isotopic with one another. A difference in atomic weight is not necessarily found between two isotopes; for radium-D and the end-product of the disintegration of radium-C_2 both have the atomic weight 210, yet they

[1] Soddy, *Chem. Soc. Ann. Rep.*, 1910, 7, 285.
[2] Soddy, *Chemistry of the Radio-elements*, 1911, I., 29.

Digitized by Google

differ entirely from each other in atomic stability, since radium-D continues to disintegrate whilst the other isotope remains stable.

At first it was believed by less progressive chemists that this conception of isotopy could be confined to the group of radio-elements and that it would not intrude into the sphere of the stable elementary forms; but the proof that the "element" lead exists in two varieties,[1] one of which has the atomic weight 206·08 while the other is found to yield the value 207·694, showed that even a common element could display isotopy.

The list of elements existing in isotopic forms has been greatly extended by the work of Aston upon mass-spectra. Using Thomson's method of positive-ray analysis, by means of which the isotope of neon was originally discovered,[2] Aston proved[3] that many "elements" are not atomically homogeneous. For example, krypton contains no less than six sets of atoms with atomic weights of 78, 80, 82, 83, 84 and 86; boron is a mixture of two types of atom, having weights of 10 and 11; silicon also contains two varieties of atoms weighing respectively 28 and 29; and chlorine appears to be a mixture of three different materials with weights of 35, 37 and 39. Mercury is a complex mixture containing atoms weighing 203 and 204 in addition to some other material ranging between 197 and 200.

Thus in the case of the very element chlorine chosen by Crookes as an example, we have now experimental proof that the "elementary material" is not homogeneous but is really a mixture of atoms which differ from each other by as much as two or even four units in atomic weight. Not only so, but in some cases the atomic weights of two elements overlap each other. For example, argon and chlorine contain atoms of the following weights:—

Chlorine	35
Argon	36
Chlorine	37
Chlorine	39
Argon	40

[1] Soddy, *Chem. Soc. Ann. Rep.*, 1913, **10**, 269; 1916, **13**, 247; Soddy and Hyman, *Trans.*, 1914, **105**, 1402; Curie, *Compt. rend.*, 1914, **158**, 1676.

[2] Thomson, *Rays of Positive Electricity*, 1913, p. 112.

[3] Aston, *Nature*, 1918, **104**, 393; 1920, **105**, 8; 1921, **106**, 828; *Phil. Mag.*, 1920, **39**, 449, 611; 1921, **42**, 436; *Trans.*, 1921, **119**, 677. A full account of Astons' methods and results is to be found in his paper in *Science Progress*, 1920, **15**, 212.

Digitized by Google

so that a distinction between argon and chlorine upon a pure atomic weight basis is impossible. If the atoms of the two gases were separated according to atomic weight and then arranged in order of increasing mass, the one element would be interspersed with the other; and the Periodic System would become impossible.

From an examination of eighteen elements by means of the mass-spectrometer, Aston[1] established the general rule that all the atomic masses measured by him were *whole numbers* on the oxygen standard.* In no case did he detect any material with a fractional atomic weight such as 35·5 or 39·8. From this he drew the conclusion that Prout's hypothesis may yet prove to be correct, since the real weights of the atoms are evidently representable by a series of whole numbers, and the fractional values which are found in chemical atomic weight determinations are due to the fact that the chemical "atomic weight" is not a physical constant but is merely the average of a mixture of various atoms having different masses and being commingled in chance proportions in the "element".

The determination of the densities of isotopic forms of lead goes to prove that the isotopes have identical atomic volumes; from which it appears that the atomic volume is a true physical constant, and the atomic volume curve thus gains additional interest.

The X-ray spectra of two isotopes appear to be identical with one another, which from the physical side lends further support to the results obtained by purely chemical methods.

The old system of elemental classification upon an atomic weight basis became even more impossible when it was pointed out by Stewart[2] that cases are known in which two elements may exist with the *same* atomic weight but with totally distinct chemical properties. For example, mesothorium-1, mesothorium-2 and radiothorium have all the same atomic weight, 228, but the first belongs to Group II.*a*, the second to Group III.*a* and the third to Group IV.*a* as far as chemical

[1] Aston, *Science Progress*, 1920, **15**, 220; *Trans.*, 1921, **119**, 677.

[2] A. W. Stewart, *Phil. Mag.*, 1918, **36**, 326.

* Hydrogen appears to be an exception to this rule, the mass of its atom corresponding to 1·008 in the mass-spectroscope results if oxygen be taken as 16.

Digitized by Google

properties are concerned. Such elements were named isobares * by Stewart, since their atoms have the same weight.

Thus upon a basis of pure experiment, apart from any theory of their origin, it is now established that the atoms of elements may be placed [1] in one or other of the following categories:—

	Atomic Weight.	Place in the Table.	Examples.
Heterobaric heterotopes .	Different	Different	Lithium and chlorine
Heterobaric isotopes .	,,	Same	Thorium and ionium
Isobaric heterotopes .	Same	Different	Mesothorium-2 and radiothorium
Isobaric isotopes . .	,,	Same	Radium-D and radium-C_2 end-product

10. *Atomic Order and Atomic Numbers.*

The evidence summarised in the last section destroyed, once for all, any attempt to rehabilitate the atomic weights as a guide to the arrangement of the elements according to a logical system. The anomalies in the case of argon and potassium turned out to be easily explicable on the assumption that each of these "elements" consisted of a mixture of more than one kind of atom, as indeed is experimentally established in numerous cases. But since the experimental evidence showed that Crookes was absolutely correct in his conjectures in 1888 as to the non-identical character of atoms in elements, the net result of the recent progress was to throw the chemist back upon Crookes' further suggestion that the places in the Periodic Table should be taken to represent not homogeneous matter but *chemically homogeneous* matter. In other words, the Table merely represented a grouping of materials according to their chemical character and had no relation to the ultimate nature of the atoms which were thus arranged within a single class.

Fortunately, at this moment, evidence came to light from another field of research which placed the Periodic System on

[1] Soddy, *Trans.*, 1919, **115**, 1.

* Pronounced *isobars*, the "e" being inserted merely to distinguish the word from the meteorological term "isobar".

Digitized by Google

a firm foundation once more. The first suggestions came from van den Broek[1] and took the form of a proposal to throw over the order of atomic weights and to choose instead the chemical sequence as the true guide to the solution of elemental problems. Thus the sequence of elements in the Table is regarded as the Atomic Order, apart altogether from any question of atomic weight.

With the conception of Atomic Order there came, naturally, the idea of Atomic Numbers which served to indicate the position of the elements in the series; but according to van den Broek these atomic numbers have a meaning apart altogether from the Periodic Table. On his view, if the elements are arranged in increasing order of number of electrons surrounding the positive nucleus of the neutral atom and numbered in order 1, 2, 3, etc., then these numbers—which are called the atomic numbers of the elements—are identical with the numbers of free electrons in the corresponding neutral atoms and also with the numbers of the places occupied by the elements in the Periodic Table when hydrogen, helium, lithium, etc., are assigned the places 1, 2, 3, etc.

By this conception, a physical meaning appears in the outlines of the Periodic System; and the recent discoveries in the mechanics of the atomic structure are linked up with the classification of the elements.

At the time it was published, van den Broek's series of atomic numbers came to a halt, perforce, somewhere in the neighbourhood of lanthanum; for after that in the series appeared the rare earth group of elements in which there was no chemical guide to help in the establishment of the atomic order. In the treatment of these substances, Mendeléef's Table had notoriously failed; and until the total number of the rare earth elements, discovered and undiscovered, had been established, it was impossible to determine the correct atomic number of a well-known element such as tantalum, which came later in the series.

At this moment, the work of Moseley upon X-ray spectra

[1] Van den Broek, *Nature*, 1911, **89**, 78; 1913, **93**, 373, 476; *Phil. Mag.*, 1914, **27**, 456; *Physikal. Zeitsch.*, 1912, **14**, 33; see also Soddy, *Nature*, 1913, **93**, 399, 452; Rutherford, *ibid.*, 423; Soddy, *Brit. Assoc. Report*, 1913, paper in Section B; Bohr, *Phil. Mag.*, 1913, **26**, 1.

Digitized by Google

was published; and with it, the whole sequence of atomic numbers was made clear.[1] When a cathode ray is allowed to impinge upon an element, an X-ray is given off by the material; and Moseley showed that the frequency of vibration of this X-ray can be expressed by the following formula:—

$$\text{Frequency} = A(N - b)^2$$

where A is a definite (fractional) multiple of Rydberg's fundamental constant for spectra; b is a numerical constant (equal to unity in the case of the K-line of the X-ray spectra); and N is the atomic number of the element under examination.

Thus by measuring the frequency of the characteristic X-ray emitted by an element it is possible to determine the element's atomic number; since the other two factors in the expression are known. In this way Moseley determined the places in the atomic order occupied by most of the known elements; and from his results it is possible to allocate the correct numbers to the remaining places in the Table. Not only so, but in the rare earth group of elements it was possible to say how many still remained undiscovered.

Moseley's work placed the conception of atomic order upon a firm experimental basis; and it served further to depreciate the value of atomic weights as a guide in classification; for it was found that the sequence of the elements as established by the X-ray method was the true chemical order and that it did not contain the anomalous inversions in the case of iodine and tellurium, etc., which were a blot upon the older mode of elemental arrangement.

[1] Moseley, *Phil. Mag.*, 1913, **26**, 1024; 1914, **27**, 703; see also Soddy, *Chem. Soc. Ann. Rep.*, 1914, **11**, 279, for further information on Moseley's unpublished results.

Digitized by Google

CHAPTER XIX.

THE ATOMS AND THE PERIODIC SYSTEM.

1. *The Atomic Numbers and Atomic Properties.*

In the last chapter it was made clear that the atomic number of an element is connected with the chemical properties of the substance on the one hand and with the characteristic X-ray spectrum upon the other; so that it brings into touch with one another the physics and the chemistry of the atomic structure. In the case of so fundamental a factor, it is not without interest to go a little deeper into the matter and see if further light can be thrown upon the subject.

When the atomic numbers are compared with some other properties of the elements, it becomes clear that it is easier to say what is independent of the atomic number than it is to find properties which go hand in hand with the atomic order.

In the first place, there seems to be no relation between the atomic number and the maximum valency exhibited by an element. The atomic numbers increase regularly from lithium to chlorine, although the possible maximum valency exhibits a periodic rise and fall throughout this series of elements. Again, in the rare earth class of elements, although the whole set are mainly trivalent and no marked periodicity in valency is shown, the atomic numbers increase from element to element just as in the previous case.

Secondly, the isotopic elements radium-B and lead have identical X-ray spectra—and therefore the same atomic number—and yet the atomic weight of the one is some seven units greater than that of the other. This seems to prove conclusively that the atomic weight and the atomic number of an atom stand in no direct relationship.

Thirdly, since the radioactive properties of radium-B and lead are entirely different, it seems indisputable that the atomic

Digitized by Google

number and the radioactive character of elements are independent properties. This is somewhat surprising, since radioactive change is supposed to have its seat in the nucleus of the atom; and it might have been anticipated that the difference between a decrepit nucleus and a stable one would have made itself manifest to the X-ray test.

In the fourth place come the chemical properties of the elements; and here the ground is somewhat shaky. What do we really understand by the chemical properties of iron? Do we mean the properties which it exhibits in the ferrous state or in the ferric condition; or is it proposed to consider all the reactions of iron as a whole? If so, what becomes of the Periodic System with its nicely graded series of periodicities in valency? Or again, consider the case of gold. Here is an element which, according to its compounds of maximum valency, ought to be placed in Group III.; yet if this were done, the atomic order would be destroyed. The most obvious chemical properties of gold do not fall into line with its atomic number; for if it be trivalent it should lie with thallium to the right of divalent mercury. Thus in order to bring the chemical properties into line with the atomic order, it is necessary to pick and choose among the properties of the element in a manner which is nothing less than arbitrary. The plain truth of the matter seems to be that after arranging the elements in the order of their X-ray spectra, we then have to select a particular set of chemical properties which will fit the Periodic System, while neglecting wilfully certain other (and possibly more characteristic) features of their chemical behaviour. It may be objected that the chemical properties of gold mark it off definitely from all other forms of matter with which we are acquainted; which is quite true. But this is not the same thing as saying that the position of gold in the X-ray atomic order is the natural position of gold among the elements.

Fifthly, there seems to be no quantitative connection between electromotive force and atomic numbers, though it has been shown that the E.M.F. of radium-E is the same as that of its isotope bismuth; and that the same holds good in the case of other isotopic groups.[1]

Sixthly, since atomic volumes vary periodically whilst

[1] Paneth and von Hevesy, *Physikal. Zeitsch.*, 1914, **15**, 797.

Digitized by Google

atomic numbers increase in regular sequence, no direct relationship can be traced between these two properties. Here again, however, it is found that isotopic elements have equal atomic volumes.* No longer true: see density of H_2^1O & H_2^2O

Thus in none of the properties mentioned above is there any obvious parallelism between the atomic properties and the atomic numbers. Light spectra and X-ray spectra appear to be the only cases in which such relations can be traced; and in the light spectra the parallelism is none too obvious.

Nevertheless, the close alliance between the atomic numbers obtained from X-ray spectra and the numbering of the places in a table drawn up, in the main, from purely chemical data cannot fail to be impressive; and it is possible that future investigations may bring to light further information which may widen our ideas on the whole subject of the arrangement of the elements.

In connection with the atomic numbers, attention may be directed to another point. A rough comparison between the atomic number of an element and the weight of the atom leads to the guess that the atomic weight is numerically double the atomic number. A closer examination of the matter, however, shows that the ratio between the two values is not constant. From helium up to calcium, the relationship W = 2N holds good almost exactly; but from scandium onwards the weight increases at a greater rate than the atomic number does. Thus at various points in the series the value of W/N is expressed by the numbers shown below:—

	O	S	Cr	Se	Mo	Te	W	U
W/N =	2·0	2·0	2·16	2·32	2·28	2·45	2·48	2·59

From these figures it is evident that no arithmetical relationship exists between the atomic number and the atomic weight —as was already obvious from the discovery of isotopes of different masses; and calculation will show that there is no readily detectable connection between the two constants. The deviation from the calculated value recalls that observed in the case of osmotic pressure, which follows van't Hoff's formula

* On the other hand elements, with different atomic numbers and different chemical properties, such as sodium and chlorine, may also have exactly equal atomic volumes.

Digitized by Google

up to a certain point and then begins to diverge from it with increasing concentration.

Turning next to the inter-relation of the atomic numbers belonging to elements of the same group, there appears to be a certain regularity in this which was detected by Rydberg.[1] Taking the inert gases as examples, their atomic numbers are 2, 10, 18, 36, 54 and 86; and these values can be expressed in the following way, which recalls Dumas' work upon the relations between the atomic weights:—

Helium	$2\,(1^3)$
Neon	$2\,(1^3 + 2^2)$
Argon	$2\,(1^3 + 2^2 + 2^2)$
Krypton	$2\,(1^3 + 2^2 + 2^2 + 3^2)$
Xenon	$2\,(1^3 + 2^2 + 2^2 + 3^2 + 3^2)$
Niton	$2\,(1^3 + 2^2 + 2^2 + 3^2 + 3^2 + 4^2)$

What is most interesting in this series is that it remains quite regular in its evolution although the group of rare earth elements comes into the sequence between xenon and niton; and in most cases the intrusion of these elements brings the general type of classification to the ground.*

In connection with the atomic order, a point of some interest suggests itself when the transitional region of the zero group is examined. In the following table, the figures give the melting-points of the elements on the centigrade scale:—

⊖				↑
Increasing	Fluorine	Neon	Sodium	Increasing
cohesion	− 233°	—	97°	cohesion
Decreasing	Chlorine	Argon	Potassium	Decreasing
negativity	− 102°	− 190°	62°	positivity
↓	Bromine	Krypton	Rubidium	⊕
	− 7°	− 169°	38°	
	Iodine	Xenon	Caesium	
	114°	− 140°	25°	

[1] Rydberg, *Phil. Mag.*, 1914, **28**, 144.

* In another paper (*J. Chim. phys.*, 1914, **12**, 585) Rydberg suggests that the elements can be arranged in five series containing respectively 1, 4, 16, 36 and 64 elements. His first series contains only the electron; the second series includes hydrogen, coronium, nebulium and helium; the third series extends from lithium to argon, inclusive; the fourth series runs from potassium to xenon; and the final series begins at caesium. Compare with this the speculations of Harkins and Hall (*J. Amer. Chem. Soc.*, 1916, **38**, 169) and Soddy's criticism of them (*Chem. Soc. Ann. Report*, 1916, **13**, 254).

Digitized by Google

An examination of the scheme shows in the first place that fluorine, chlorine and bromine have less molecular cohesive power than sodium, potassium and rubidium; for the melting-point indicates the temperature limit at which the organised solid collapses into the irregular liquid distribution of molecules. Thus in the lower members of the series, the electronegative elements have less cohesion than the electropositive ones. This rule extends to the elements immediately lying above and below this set in the atomic order, since the "negative" elements nitrogen and oxygen are gaseous, whilst the electropositive magnesium and aluminium are solids. As the atomic number increases, however, the relationship of the cohesive powers is inverted; for iodine melts nearly ninety degrees higher than caesium.

The two arrows in the scheme serve to bring out another point. Fluorine is the most strongly electronegative element known and the negativity diminishes steadily as we pass down the halogen group towards iodine, which shows what might almost be called basic properties in such compounds as diphenyl-iodonium hydroxide, $(C_6H_5)_2 : I . OH$. Conversely, the basicity of the alkali metals decreases as the atomic number falls. Thus in the halogen group increase in cohesive power goes hand in hand with decreased negativity; whilst in the alkali metals an increase in cohesive power accompanies decreased positivity.

From these facts, three conclusions may be drawn. The cohesive power which holds the atoms of a metal together obviously has no direct connection with mere positive or negative character; or if there be such a connection, it is completely overborne by some other factor. Secondly, the more a negative element approaches a state of balance between positive and negative character, the greater becomes its cohesive power and the higher its melting-point. In this connection the case of carbon at once suggests itself, since that element yields an acidic oxide and yet combines equally well with chlorine or with hydrogen, thus showing an amphoteric character; and, as we know, carbon is one of the most infusible of the elements. Finally, if the positive and negative characters could be so intimately blended as to neutralise each other instead of existing side by side as in carbon, it might be expected that the

Digitized by Google

cohesive power of the element would be negligible. The low melting and boiling-points of the inert gases suggest that in their case this condition is fulfilled.*

It appears, then, that the extremes of electronegative or electropositive character lead to slight intermolecular cohesion; complete neutrality is also accompanied by low cohesive power; but amphoteric character goes hand in hand with great cohesive capacity. This cannot fail to suggest that the force of cohesion, if it be chemical, depends upon an unlikeness in the valencies of the atoms of the element involved; and this idea is supported by the fact that the alkali metals which show most cohesive power are capable of uniting with both chlorine and hydrogen, whereas fluorine, though it gives a hydrogen compound, will not unite with chlorine.

2. *Some Resemblances not Expressed in the Periodic Table.*

Although Mendeléef's form of the Periodic Table, with its sub-Groups A and B, produces at first sight a satisfying solution of the problem of elemental classification, it must be borne in mind that it fails in several respects; and that its somewhat illusive simplicity is apt to mislead us in some ways. In the first place, it fails completely to deal with the group of rare earth elements; for if the symmetry of the Table be maintained, there are more blanks in it than can be filled by the number of elements predicted from the X-ray spectra series; whilst if all the rare earth elements be allotted to a single space in the Table, then the spectrum evidence must be neglected altogether, since it ascribes separate places to each member of the rare earth group.

There is a lesser objection to be brought against the Mendeléef Table which deserves a brief notice here. While the Mendeléef system brings out a very large number of resemblances between the properties of elements of the same group in many cases, it places in juxtaposition some elements which do not resemble each other except in the most superficial manner, and at the same time it separates from one another certain elements exhibiting resemblances which are often closer than those shown by members of the A and B sub-Groups of a

* The fact that the melting-point of helium is lower than that of hydrogen is especially striking in this connection.

Digitized by Google

single group in the Table. A few concrete examples may serve to direct the attention of the reader to this point.

Beginning with Group I., we find included in it the two sub-groups: (1) lithium, sodium, potassium, rubidium, caesium; and (2) copper, silver and gold. It is safe to say that a chemist acquainted only with the chemical and physical properties of the elements and ignorant of the Periodic System would hardly be likely to classify these two sub-groups together.

Taking valency under consideration in the first place, the alkali metals form chlorides of the type R . Cl and must therefore be regarded as monovalent; but in sub-Group B, the matter assumes a different aspect. Copper yields both cuprous and cupric salts, in the latter of which the metal must be divalent; and if the formula for cuprous chloride be Cu_2Cl_2, copper is divalent in this case also. Silver appears to be like the alkali metals in that it exhibits only monovalency in its chloride. Gold, on the other hand, exhibits monovalency in AuCl and trivalency in $AuCl_3$.

Turning to solubility, the difference between the two sub-groups is even more marked. While the chlorides of the alkalis are all readily soluble in water, the chlorides derived from monovalent silver and gold are insoluble, as is also cuprous chloride.

A marked difference is to be found in the atomic volumes, since the alkali metals have the largest volumes of all the elements, whilst the elements of the copper sub-group lie at the troughs of the Atomic Volume Curve.

In purely chemical characteristics, similar differences are exhibited. All the alkali metals attack water rapidly at ordinary temperatures; but the action of copper, silver and gold under the same circumstances is almost negligible. The alkali metals form both normal carbonates and bicarbonates;* whilst in the case of copper and silver no bicarbonate is known and copper yields a basic carbonate in contradistinction to the acidic bicarbonates of the alkalis.

When the actual resemblances between the members of the two sub-groups are examined, it will be found that they are

*Note the resemblance to calcium in this, a resemblance which is strengthened in the case of lithium owing to the comparative insolubility of its carbonate.

Digitized by Google

few in number and not particularly striking. The double salt formation of the alkalis may find its parallel in the complex-forming capacity of copper and its analogues. Some cases of isomorphism between the salts of the members of the two sub-groups may also point to an innate resemblance in character.

On the whole, therefore, the juxtaposing of copper, silver, gold and the alkali metals is certainly not satisfying in its results, as far as the bringing out of chemical resemblances goes. It may be well to ascertain if there are not closer kinships which are masked by the arrangement of Mendeléef's Table.

Let us take copper as an example and see whether some other elements do not resemble it more closely than the alkali metals do. Since it occurs in the divalent form, we may begin by examining the metals of Group II. in order to find among them any possible parallel to the properties of copper. The sub-Group A may be omitted from consideration, since Ca, Sr and Ba do not show any clear relationship with copper. This leaves us with beryllium and magnesium, zinc, cadmium and mercury.

The oxides BeO, MgO and ZnO have close chemical relationships with CuO; and all four metals yield insoluble hydroxides. The formation of basic carbonates is characteristic of the whole series of elements. Zinc, cadmium and mercury, like copper, form insoluble sulphides. When the resemblances between copper and mercury are considered, they are very close indeed. While copper forms two oxides, Cu_2O and CuO, mercury yields Hg_2O and HgO. Again, in the case of the chlorides, Cu_2Cl_2 and Hg_2Cl_2 are insoluble in water whilst $CuCl_2$ and $HgCl_2$ are readily soluble in either water or alcohol. Both copper and mercury form basic sulphates, carbonates and nitrates. With ammonia, the salts of the two metals give rise to a series of complex ammoniacal derivatives. From these facts, it is clear that, logically, copper has associations with other elements much closer than those which unite it with the alkalis.

But this type of resemblance does not even cease with Group II., for thallium, in the third group, also shows a remarkable kinship with copper. Thus parallel to cuprous hydroxide we find thallous hydroxide, both of which are obtainable by precipitation; cuprous sulphide, Cu_2S, finds its analogue in

Digitized by Google

thallous sulphide, Tl_2S, both compounds being insoluble in water. There are other resemblances which it is not necessary to mention in detail.

Curiously enough, thallium also displays resemblances to the alkali metals. For example, the properties of thallous carbonate, Tl_2CO_3, are very close to those of lithium and sodium carbonates. In fact, thallium carbonate might also be regarded as a "bridge" between the carbonates of lithium and sodium. Again, the sulphate and phosphate of thallium in the monovalent condition are isomorphous with the corresponding potassium compounds; and this resemblance persists even into the stage of the alums.

Silver and monovalent thallium are also related to one another by some properties. The chlorides, bromides and iodides of the two metals can be prepared by precipitation; and thallous chloride is photosensitive like silver chloride. The fluorides of the two elements are very soluble in water. Both metals yield black insoluble sulphides. Silver sulphate and thallous sulphate are both sparingly soluble in water and their solubilities are increased by the addition of dilute sulphuric acid. Thallous nitrate and silver nitrate occur in the rhombic form and each passes into a new crystalline form on heating. The two phosphates, Ag_3PO_4 and Tl_3PO_4, are obtainable by precipitation.

Between gold and thallium there is also a certain resemblance, closer than that which exists between gold and the alkali metals. Both gold and thallium yield oxides of the type R_2O and R_2O_3. The hydroxides have the compositions corresponding to R.OH and $(ROH)_3$. When heated, both auric and thallic hydroxides undergo changes resulting in AuO(OH) and TlO(OH) respectively. Aurous chloride and thallous chloride are both very slightly soluble in water, whilst auric and thallic chlorides are deliquescent. The sulphides of gold and thallium in the monovalent condition resemble each other in several respects.

The foregoing facts are quite sufficient to bring out two points. In the first place, copper, silver and gold have alliances with metals in the second and third groups which are much more striking than any resemblances we can suggest between them and the alkali metals. Secondly, thallium

Digitized by Google

exhibits an extraordinary likeness to the alkali metals on the one hand and to copper, silver and gold on the other, the resemblances in each case covering the very properties in which the alkalis and the copper group differ most from each other. The Table in its present form suggests nothing of this character; and to this extent it must be regarded as an incomplete representation of the chemical facts.

If, instead of comparing copper, silver and gold with the elements lying above them in the atomic order, we turn to those which precede them in this arrangement, a different state of things is to be found. Only a few resemblances exist, and these are physical rather than chemical. Nickel and copper both occur naturally as NiO and CuO respectively. Both yield hydroxides of the type $R(OH)_2$ which are insoluble in water but soluble in ammoniacal solutions. Each element forms two sulphides of which the lower is obtained by heating sulphur with the element, whilst the higher sulphide is prepared by precipitation. Addition of an alkali carbonate produces basic carbonates from solutions of nickel or copper salts. With nitrogen peroxide, both metals give "nitro" derivatives, $Cu_2(NO_2)_2$ and $Ni_2(NO_2)$.

The resemblances between palladium and silver are almost entirely confined to the physical properties, since palladium is divalent while silver is definitely monovalent. Gold and platinum have a certain chemical kinship owing to the occurrence of a trivalent form of platinum; but there is no marked similarity between the two elements. It has been suggested[1] that the trivalency of gold enables this element to take its place naturally in the series—

$$PtCl_4 \quad AuCl_3 \quad HgCl_2 \quad TlCl$$

and this view seems to hint that in the Periodic Table too much stress has been placed upon some displays of valency to the detriment of others which on the surface do not agree with the system of classification.

Let us now turn to the elements of Group II. in the Table. Here all appears to be quite in order, for with the exception of mercury (which has already been dealt with above) the metals behave normally as regards valency. An examination

[1] Caven and Lander, *Inorganic Chemistry*, 1906, p. 51.

Digitized by Google

of the properties of beryllium, however, brings out immediately a strong resemblance between it and aluminium. Both metals yield gelatinous hydroxides which can be prepared by precipitation and which are soluble in acid or alkali; neither yields a normal carbonate by precipitation; and both metals attack alkaline solutions with the evolution of hydrogen. Some attempts have been made to draw a parallel between lead and barium; but with the exception of the insolubility of the two sulphates, there seems to be little real likeness between them.

In Group III., boron offers a remarkable resemblance to silicon in Group IV. and to some extent resembles carbon also. Thus boron and silicon are prepared by analogous methods (reduction of fluoride of element by means of metals or reduction of potassium boro- or silico-fluoride with potassium). Neither boron nor silicon unites direct with the alkali metals. The most striking parallelism is to be found in the hydrides of the elements; for although boron is placed in Group III., its hydrogen derivatives show it to be closely associated with silicon and carbon, as the following list proves:—

B_2H_6	B_4H_{10}	B_6H_{12}
C_2H_6	C_4H_{10}	C_6H_{12}
Si_2H_6		

From its position in Group III., boron might have been expected to yield the hydride BH_3; but the place of this substance is taken by B_2H_6 which is a colourless gas like the corresponding ethane and silico-ethane.

Omitting Groups IV. and V. and passing to Group VI., we reach chromium, which seems to have collective properties belonging to many other elements. The oxide CrO, when in the hydrated form $Cr(OH)_2$, is feebly basic and recalls the behaviour of the corresponding compounds MgO and ZnO. The sesquioxide, Cr_2O_3 resembles Al_2O_3 and Fe_2O_3 in its faculty, when hydrated, of dissolving in either acids or alkalis; and in the power of producing alums like chrome alum, which are exactly analogous to the aluminium alums. Chromic oxide, CrO_3, has many analogies with the oxides of its group-congeners, tungsten and molybdenum. Chromous sulphate, $CrSO_4$, $7H_2O$, forms a double sulphate with potassium sulphate which is exactly analogous to the double salt of potassium and ferrous sulphates.

Digitized by Google

Group VII. provides in manganese an element which is probably one of the most extraordinary of the chemical chameleons. MnO is a basic oxide yielding manganous salts such as $MnSO_4$ which forms a double salt with potassium sulphate, isomorphous with the double sulphates of potassium sulphate and magnesium, or ferrous sulphate. Thus manganese may be regarded as related to iron and magnesium. Manganous hydroxide, $Mn(OH)_2$, is prepared by the precipitation of a salt by means of caustic alkali, just as cuprous hydroxide is obtained; and, like cuprous hydroxide, the manganous derivative readily oxidises in air. On this account a relationship can be traced between manganese and copper. Again, the manganates are isomorphous with the sulphates and chromates, which brings out an analogy between manganese and the elements of Group VI. Finally, the resemblances between manganese and the halogens appear to be confined to the case of the permanganates, which are isomorphous with the perchlorates; but the parallel ends here, since there is no resemblance between oxides lower than Cl_2O_7 and Mn_2O_7.

The following table will serve to bring out the very numerous associations which manganese has with the other elements:—

Manganese Compound.	Analogous Compounds.		
MnO	FeO		
Mn_2O_3	Fe_2O_3		
MnO_2	CrO_2		
Mn_2O_7	Cl_2O_7		
$Mn(OH)_2$	$Fe(OH)_2$	$Mg(OH)_2$	$Cu(OH)_2$
$MnCO_3$	$FeCO_3$		
K_2MnO_4	K_2SO_4	K_2CrO_4	
$KMnO_4$	$KClO_4$		
$MnSO_4, 7H_2O$	$FeSO_4, 7H_2O$	$MgSO_4, 7H_2O$	
$MnSO_4, K_2SO_4, 6H_2O$	$FeSO_4, K_2SO_4, 6H_2O$	$MgSO_4, K_2SO_4, 6H_2O$	
$Mn_2(SO_4)_3, K_2SO_4, 24H_2O$	$Fe_2(SO_4)_3, K_2SO_4, 24H_2O$	$Al_2(SO_4)_3, K_2SO_4, 24H_2O$	

Manganese gives rise to no less than five oxides, MnO, Mn_2O_3, MnO_2, MnO_3 and Mn_2O_7; and if it be permissible to select AuCl rather than $AuCl_3$ as the typical compound in the case of gold, it is evident that some defence might be urged in favour of placing manganese in the second, third, fourth or sixth groups just as logically as in the usual position in the seventh group, where it has, as a matter of fact, very few resemblances to its neighbours.

Digitized by Google

Enough has now been said to show clearly that the Periodic Table by no means exhibits all the similarities between the elements; and, on the other hand, it brings together elements which are very unlike each other, as in Group I. It is evident that Mendeléef's classification is too rigid—as the case of the rare earth elements shows plainly—and if a system less liable to criticism is to be evolved, it will have to take on a more flexible character. This question, however, may be postponed to a later section of this chapter.

3. *The Rare Earth Elements.*

The occurrence of the rare earth group of elements is one of the most puzzling facts which research has brought to light in inorganic chemistry; for here, in the very middle of the Periodic System, are found no less than seventeen elements which up to the present have defied all efforts to bring them into a satisfactory relation to the remaining types of elementary matter. In earlier days, it was always possible to assume that further investigation would reveal fresh members of the group and that the properties of these new materials might serve as clues to a proper classification; but the work of Moseley upon the X-ray spectra of the elements has made it clear that only one more rare earth element remains to be discovered; and it seems hardly likely that its character will enable us to see very much further into the maze than we do at present.

According to Moseley's results,[1] the atomic numbers of the rare earth elements are those shown in the table below. The element corresponding to the number 61 is still undiscovered (1921):—

Atomic Number.		Atomic Weight.	Atomic Number.		Atomic Weight.
57	Lanthanum .	139·0	65	Terbium . .	159·2
58	Cerium . .	140·25	66	Dysprosium .	162·5
59	Praseodymium	140·9	67	Holmium .	163·5
60	Neodymium .	144·3	68	Erbium . .	167·7
61	Undiscovered .	?	69	Thulium . .	168·5
62	Samarium .	150·4	70	Ytterbium .	173·5
63	Europium .	152·0	71	Lutecium .	175
64	Gadolinium .	157·3	72	Celtium . .	?

[1] Moseley, *Phil. Mag.*, 1913, **26**, 1024; 1914, **27**, 708; see also Soddy, *Chem. Soc. Ann. Reports*, 1914, **11**, 279, for further information.

Digitized by Google

A glance at the ordinary form of the Periodic Table will suffice to show how anomalous this rare earth group is. The first two Periods, helium to fluorine and neon to chlorine, contain eight elements each; the next two Periods, argon to bromine and krypton to iodine, eighteen elements each; so that apparently a fresh type of element—the groups scandium to zinc and yttrium to indium—has been inserted into the system in the second pair of Periods. By analogy, it might be expected that in the next two Periods, beginning with xenon and niton respectively, yet another fresh type of element would make its appearance; and at first sight the rare earth group seems to fulfil the expectation, since its occurrence lengthens the xenon period to thirty-two elements.

At this point, however, objections arise. In the first place, the interpolated elements in the second pair of periods have direct analogies with the corresponding elements of the first two periods: scandium and yttrium resemble aluminium; and chromium and molybdenum show some likeness to sulphur in their compounds. In the case of the rare earth elements, the whole group shows a marked trivalent character and there is nothing even remotely resembling a halogen to be detected among them. Further, if the rare earth group were a normal development in the elementary grouping, it should be repeated in the next long period, just as zirconium repeats the type of titanium, with modifications, in the second pair of periods.[1] Actually, however, the period beginning with niton shows no trace of a rare earth group in it; for the atomic number of thorium is ninety, which allows no intercalation of a "rare earth group" at all. Nor is the matter evaded by assuming that the various isotopes make up the "rare earth" group, for the number of them already known raises the figure far above the required thirty-two.

We are thus left with this mysterious class of elements, all closely resembling each other in properties, which has to be fitted into the scheme of elemental classification in some way or other. Three methods of dealing with them have been suggested: (1) to place them all in a single space

[1] Soddy, *Chem. Soc. Ann. Reports*, 1916, **13**, 254.

Digitized by Google

in Group III.; (2) to regard them as a "bridge" between barium and tantalum outside the ordinary tabular arrangement; and (3) to distribute them among the ordinary groups in a more or less systematic manner. These three proposals may be dealt with in turn:—

1. The suggestion of grouping all the rare earth elements into a single space in the table is one which nowadays has few supporters. The rare earth elements, though difficult to isolate from one another, are not by any means chemically inseparable; and they have no claim whatever to be regarded as isotopic with each other. The frequencies of their X-ray spectra run in an order as regular as that of the ordinary elements and since each of them is thus possessed of a definite atomic number, it seems evident that each must be granted an individual place in any arrangement of the elements which we draw up.

2. The second proposal—to place the rare earth group outside the table altogether—is a complete negation of our laboriously-acquired views on the Atomic Order. Since the Atomic Numbers run consecutively from barium to tantalum there is no argument for the creation of a hiatus in the middle of the series.

3. These two suggestions being thus put aside, there remains only the hope that the rare earth elements can be distributed in some way among the others. Various attempts have been made to do this; but it cannot yet be claimed that the efforts have been entirely successful. The ordinary Mendeléef Table is placed out of court at once, on account of the disparity between the number of blank spaces in it and the number of the rare earth elements known to exist. Also, neither the halogen nor the inert gas group is represented by anything we are acquainted with among the rare earth elements, although Mendeléef's system would demand the existence of two such types. Evidently, then, in order to fit the rare earths into the elemental classification, the rigidity of the Mendeléef arrangement must be discarded.

The following attempt[1] seems to be the most successful

[1] Stewart, *Recent Advances in Physical and Inorganic Chemistry*, 1920, p. 255.

Digitized by Google

up to the present, though it is probably open to improvement. Since the rare earth elements, with the exception of cerium, praseodymium and terbium, are all trivalent, they must be placed in association with other elements which at least show trivalency, no matter what their other valency powers may be. In the period beginning with rubidium, the series of elements from yttrium to rhodium show this capacity for trivalency; and in the set: tantalum, tungsten (75), osmium, iridium, platinum, the possibility of obtaining an unbroken series of "trivalent" compounds is broken at iridium, since platinum yields no trivalent derivatives. Logically, therefore, the rare earth group should be placed somehow in conformity with these "trivalent" elements; and the following seems to fulfil the requirements of the case:—

Rb	Sr	Y	Zr	Cb	Mo	—	Ru	Rh	Pd	Ag
Cs	Ba	La	Ce	Pr	Nd	—	Sm	Eu		
		Gd	Tb	Dy	Ho	Er	Tm	Yb		
		Lu	Ct	Ta	W	—	Os	Ir	Pt	Au
—	Ra	Ac	Th	UX_2	U	—	—	—	—	—

It will be noticed that this arrangement is symmetrical and requires exactly the proper number of rare earth elements which is predicted by the X-ray spectra measurements. Further, the stable oxide of cerium is CeO_2 which is parallel to ZrO_2 and ThO_2; whilst terbium also departs from the normal trivalency of the rare earth elements. In the next column to the right, praseodymium likewise furnishes an exception to the usual trivalent character, forming the oxide PrO_2 which can be paralleled by VO_2, CbO_2 and TaO_2, all of which resemble it physically. At the right hand of this line, europium forms two chlorides, $EuCl_2$ and $EuCl_3$, which are paralleled by $IrCl_2$ and $IrCl_3$. There is other evidence in favour of the arrangement; but it is unnecessary to enter into it here. Even at the best, as can be seen, the rare earth elements can be accommodated in the elemental classification only by diverging widely from the symmetry of the Mendeléef system; which goes to show that this symmetry is not in accordance with truth.

Digitized by Google

4. *The Position of Hydrogen.*

While it is comparatively simple to arrange most of the elements in such ways as to bring out the resemblances and differences between them, it has been found almost impossible to discover the proper position of hydrogen in any of these systems. This is perhaps not remarkable, if hydrogen be regarded as the lowest member of the elemental series; for in the homologous series of organic chemistry the lowest member always presents certain abnormalities in its properties which serve to differentiate it in character from its congeners. It is not without interest to examine the properties of hydrogen and see, if possible, what its natural alliances are.

Since hydrogen is the typical monovalent element which is used as a gauge for the valency of most of the other elementary forms of matter, it is clear that it must naturally be allied to either of the two monovalent groups: the alkali metals or the halogens. We may therefore compare its character with that of an alkali metal and that of a halogen and see how far the analogy can be stretched in order to include hydrogen in either of these categories.

In the first place, hydrogen may be compared with metals such as lithium or sodium. Like them, it yields strongly electropositive ions; and in the ionic form its character closely resembles that of an alkali metal. Like the alkali metals, it forms stable and highly ionisable compounds with the halogens; and in general it combines more readily and more firmly with non-metallic than with metallic elements.

A comparison between hydrogen and the halogens, on the other hand, brings out the following points: When liquefied and solidified, hydrogen resembles the halogens and shows no sign of metallic character.[1] Solid hydrogen is much less like a metal than iodine is. Further, the boiling-point of hydrogen appears to place it along with the halogens rather than with the alkali metals; for as can be seen from the following table, it fits naturally into the series of the halogens; whereas in order to harmonise with the alkali metals it would require to have a boiling-point higher than red-heat:—

[1] Dewar, *Compt. rend.*, 1899, **129**, 451.

Digitized by Google

BOILING-POINTS.

Hydrogen	− 252·5°		
Fluorine	− 185°	Red heat	Lithium
Chlorine	− 33·6°	877·5°	Sodium
Bromine	+ 59°	757·5°	Potassium
Iodine	+ 175°	696°	Rubidium
		670°	Caesium

Another resemblance between the halogens and hydrogen lies in the fact that all of them in the gaseous state have diatomic molecules, whereas the alkali metals are monatomic under the same conditions. Then again, if hydrogen were akin to the metals, it might be expected that the metallic hydrides would behave like intermetallic compounds and act as good conductors of electricity; whereas in practice it is found that they do not conduct.[1] A study of lithium hydride[2] shows it to be a close analogue of lithium chloride in crystalline form, heat of formation, atomic heat, atomic volume, colouring by ultra-violet light and other properties. In the hydrocarbons, hydrogen can be replaced quite readily by chlorine, but not by atoms of the alkali metals.

In addition to this purely experimental evidence, the halogen relationship is supported also by an argument from the atomic order. If hydrogen has the atomic number 1, it must immediately precede helium; and this position would place it in the halogen column above fluorine.

From the evidence given above, it is clear that whether hydrogen be placed in the one or the other of the two possible groups, its position will be anomalous in some respects. In its chemical properties, it appears to lean toward the metallic side; but its physical character tends to bring it into line with the halogens. It seems impossible to place it properly in the present periodic system; and the proposal of Schmidt,[3] which will be dealt with later in this chapter, has much to recommend it.

5. *Some Atomic Volume Problems.*

While atomic weights have lost their original importance as guides to classification, atomic volumes appear to have gained

[1] Moissan, *Compt. rend.*, 1903, **136**, 591.
[2] Nernst, *Zeitsch. Elektrochem.*, 1920, **26**, 323.
[3] See p. 365.

Digitized by Google

in interest owing to the work which has been done upon the varieties of lead from radioactive sources. Lead from thorium and lead from uranium have different atomic weights and different densities; but when the atomic volumes of the two types are calculated, they are found to be identical.[1] This is perhaps a slender basis for generalisation, but if it be adopted, it would appear that in the atomic volume we have a true physical constant which is the same for all isotopes. It is therefore of considerable interest to look more closely into the nature of atomic volumes; and it will be found that they present many points of a very suggestive nature.

It is, of course, more than doubtful whether the numbers which we use to express atomic volumes are absolutely correct; for temperature and pressure both enter into the problem and up to the present no uniform corrections have been made for the influence of these factors. All that we have obtained are rough approximations to a standard atomic volume. Nevertheless these approximations exhibit certain regularities which are of the greatest interest. Only one or two points can be dealt with here; but others will be apparent if a close study is made of the atomic volume curve at the end of this book.

In the first place, as Lothar Meyer[2] pointed out, it is remarkable that elements with similar atomic volumes exhibit totally different properties according as they are situated upon the rising or the falling branch of the atomic volume curve. Thus sodium and chlorine have an atomic volume of 23·7; but sodium represents a maximum of the graph whereas chlorine is on an upward branch. Columbium and cadmium furnish another example, since they have identical atomic volumes, 13·0; but here columbium is on the down-grade slope whilst cadmium lies on the next upward gradient.

A possible explanation of this is to be found in the electronic theory of matter. If it be assumed that atoms consist of a central positive nucleus containing charges equal in number to the atomic number and surrounded by negative electrons sufficient to make the whole system electrically neutral, then evidently the "atomic volume" represents the sphere occupied by the negative electrons. A large atomic volume implies that

[1] Soddy, *Nature*, 1917, **98**, 469.

[2] Lothar Meyer, *Modern Theories of Chemistry*, 1888, p. 125.

Digitized by Google

some of these electrons are far removed from the central nucleus; a small atomic volume corresponds to a more compact grouping. Further, a metallic atom—since it gives rise to a positive ion—must be able to part with an electron readily; whereas a halogen atom—since it picks up an electron on ionisation—must be capable of attracting negative charges from outside the atomic sphere. Now apply these ideas to the cases of sodium and chlorine. In each case the outermost negative electrons must be at the same distances from the central nuclei, since the atomic volumes are identical in the two elements. But in the case of sodium, the central nucleus contains eleven positive charges whereas in the case of chlorine there are seventeen positive charges in the nucleus. Obviously the pull of the central nucleus upon a negative electron outside the system will be strong in the case of chlorine and weaker in the case of sodium; and, on the other hand, the attraction of an external positive nucleus (another atom) will remove an electron much more readily from a sodium than from a chlorine atom. This conception, therefore, serves to account for the ionic character of these elements.

The conception of a true Atomic Order gains support from another observation made by Lothar Meyer;[1] for he pointed out that the properties of an element can be inferred from its position on the atomic volume curve and that this position depends upon the nature of the preceding and succeeding elements in the series. For example, an element is easily fusible or volatile if it possesses an atomic volume larger than that of the preceding element with a lower atomic weight; and, conversely, if the atomic volume of an element is not larger than that of its predecessor, then the element will be fusible or volatile only with difficulty. Thus, in addition to the mere sequence of elements suggested by the X-ray spectra, there is a further influence to be taken into account, depending upon the ratio between the atomic volumes of two successive members of the series.

Again, examination of the atomic volume curve will bring out the fact that a marked change in inclination corresponds to a perceptible difference in elemental properties. The passage from the electronegative to the electropositive type of element is

[1] Lothar Meyer, *Modern Theories of Chemistry*, 1888, pp. 132, 148 ff.

Digitized by Google

paralleled by a marked point of inflection in the curve; though, curiously enough, this point of inflection does not correspond to the positions of the inert elements as might have been expected. Since this change of inclination is only a graphic expression of the relative volumes of the successive elements, it is clear that here also there is a certain sequence in the arrangement.

The same peculiarity is traceable when it is noted that electropositive elements occur on the descending branches and at the troughs of the curve, whereas elements with places on the ascending lines on the right of each wave are electronegative in character. Thus if we know the atomic volumes of three successive elements and no more, we can still infer the character of the middle element in the trinity.

Mendeléef was a firm believer in the inhomogeneity of the elements; but to Lothar Meyer the existence of sixty or more entirely different forms of primordial matter seemed highly improbable.[1] In his view, there lay, below the range of atomic magnitudes, a series of smaller particles from which the atoms were built up; so that he had evidently reached out in his speculations toward the point to which modern experiment has brought the chemist of the present generation. With this conception in his mind, Lothar Meyer regarded atoms as aggregates formed from one and the same type of material and differing from each other only in their masses; and in the atomic volume curve we have an index of the influence produced by this change in mass.[2] When the problem is looked at from this point of view, the importance of the relationships illustrated above will be more clearly traceable. If, instead of "mass" we read "number of free positive charges in the atomic nucleus," we can convert Meyer's suggestion into modern language; and in this form it will be found to provide fruit for considerable speculation when taken in conjunction with the characteristics of the atomic volume curve. No thorough attempt has yet been made to deal with the curve of atomic volumes from the standpoint of the electronic theory of matter; and there seems to be little doubt that this field is a much more promising one than that offered by the Periodic Table. Electronic functions must govern the physical properties of matter as well as the chemical ones; and in the

[1] Lothar Meyer, *Modern Theories of Chemistry*, 1888, p. 118.

[2] Lothar Meyer, *Annalen* (*Suppl.*), 1870, 7, 358.

Digitized by Google

periodicity of the atomic volume curve there is expressed a multitude of peculiarities which offer a field of investigation wider by far than that contained in Mendeléef's Table.

6. *The General Arrangement of the Periodic Table.*

The evidence brought forward in the foregoing sections proves that the Mendeléef Table not only suffers from certain drawbacks but is actually, in the case of the rare earth elements, irreconcilable with the known facts. It breaks down as certainly, though not so extensively, as the old triad system of Doebereiner; and just as the triads marked a stage on the road toward the Mendeléef arrangement, the latter in its turn merely represents a step toward some wider generalisation which up to the present has eluded our minds. While awaiting the revelation of this future classification, it may be worth while to examine the facts once more while trying, if possible, to avoid being influenced by Mendeléef's views.

In the first place, the atomic order of the elements must be retained in some form or other, since this evidently represents their natural sequence. Secondly, as far as possible, close resemblances between sets of elements must be represented by adjacency in the arrangement; whilst there must be a periodicity throughout the system.

The following arrangement appears to bring together the greatest possible numbers of similar elements while separating from each other to some extent those classes which owe their resemblances to identity in valency rather than to actual likeness in chemical character:—

																	He
Li										Be	B	C	N	O	F	Ne
Na										Mg	Al	Si	P	S	Cl	A
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
Rb	Sr	Y	Zr	Nb	Mo	—	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	X
Cs	Ba	La	Ce	Pr	Nd	—	Sm	Eu									
		Gd	Tb	Dy	Ho	Er	Tm	Yb									
		Lu	Ct	Ta	W	—	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	—	—	Nt
—	Ra	Ac	Th	Ux_2	U												

In this arrangement, magnesium and beryllium are classed along with zinc, cadmium and mercury on the ground that all

Digitized by Google

of these elements yield alkyl derivatives which are not formed by calcium, strontium and barium. The rare earths are placed as shown, upon the grounds given in a previous section.

An examination of this scheme will reveal several points of interest. In the first place, all the metals which yield coloured chlorides in their highest stage of valency are included within the heavy line; so that these colorogenic elements form a compact group in the centre of the system.

Again, the elements forming the A and B sub-groups of the Mendeléef Table are here separated from each other and are thus allowed to manifest their individuality better than the Mendeléef system permits. For instance, since arsenic, antimony and bismuth all form hydrides like nitrogen and phosphorus, it seems reasonable to classify these five elements together whilst differentiating between them on the one hand and the non-hydride-forming class of vanadium, etc., on the other. Again, the metals titanium, zirconium, etc., form no alkyl derivatives and are properly separated from carbon, silicon, germanium, etc., which do yield alkyl derivatives.

When the electrochemical character of the elements is examined, it will be found that the arrangement given above brings out a peculiar relationship which is concealed if the Mendeléef Table be adopted. Fig. 36 shows approximately the periodic variation of electro-affinity with the atomic weight.[1] The diagram is divisible into two halves (by an ordinate at 9) such that each is roughly symmetrical with the other.* The crossing of the four curves just beyond manganese finds its counterpart in the second crossing between 13 and 14; and the dip at chromium is copied in the second half by the summit between 12 and 13. At the two extremes lie the alkali metals and the halogens; and the curve as a whole is approximately represented in its rise and fall by the following scheme:—

\+ − + − + −

which is obviously symmetrical about the centre.

Finally, this scheme concords with the Curve of Atomic Volumes better than the Mendeléef Table can do. A comparison

[1] Modified from Abegg, *Zeitsch. anorgan. Chem.*, 1904, **39**, 867.

* This is best seen by imagining the left half of the curve revolved through 180° about an ordinate at 9. In its new position this half of the curve is approximately the mirror-image of the right-hand half of the curve.

Digitized by Google

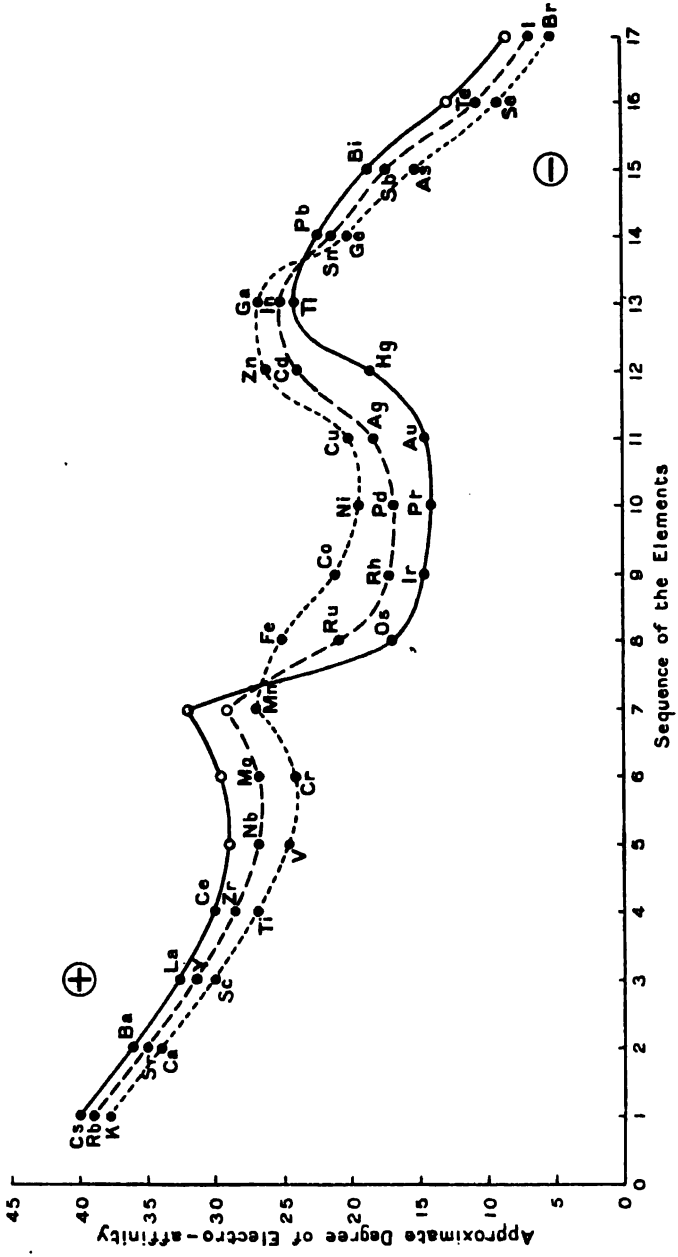


Fig. 36.

Digitized by Google

between the above arrangement of the elements and Lothar Meyer's Curve will show that the left-hand half of the lines corresponds to the descending branch of the corresponding wave in the curve; whilst the right-hand half parallels the ascending section of the curve. The break in the arrangement at the rare earth elements has its counterpart in the change of gradient in the curve at this point.

In addition to plane representations of the Periodic System, various attempts have been made to express the relations between the elements by means of three-dimensional spiral models.[1] Of these the simplest is that suggested by Soddy [2] (Fig. 37). As can be seen from the diagram, the A and B sub-groups are here placed on opposite sides of the axis; and the sharp transition in properties around the argon group is depicted by means of the peaks in the curve, whereas the gradual change in properties through iron, nickel and cobalt finds its parallel in the smoother transition at the lower parts of the diagram.

The form of table printed on p. 367 is due to Schmidt.[3] Inspection will show that it is divided into four parts, each of which Schmidt regards as a stage in the evolution of the elements from a primary material. The Primary System contains (*a*) the "astronomical" elements, *i.e.*, those which we know only through certain unidentified lines in the stellar spectra; (*b*) the so-called "proto-metals" of Lockyer,[4] which he supposes to be finer forms of the ordinary elements; (*c*) hydrogen. Thus in this arrangement hydrogen is not supposed to belong to the ordinary table at all but finds its place with the sidereal gases.

In the Secondary System, the members show sharp chemical individuality, and they are divisible into two different electrochemical groups with the inert gases interleaved between the positive and negative types.

Passing to the Tertiary System, the differences in electrochemical nature between the elements become less marked than in the Secondary System; the clear distinction between metals and non-metals disappears and all the members show some metallic properties.

[1] Crookes, *Chem. News*, 1886, **54**, 115; *Trans.*, 1888, **53**, 487; Harkins and Hall, *J. Amer. Chem. Soc.*, 1916, **38**, 169.

[2] Soddy, *Chemistry of the Radio-elements*, 1914, Part II., p. 9.

[3] Schmidt, *Zeitsch. physikal. Chem.*, 1911, **75**, 651.

[4] See Lockyer, *Inorganic Evolution*, 1900.

Digitized by Google

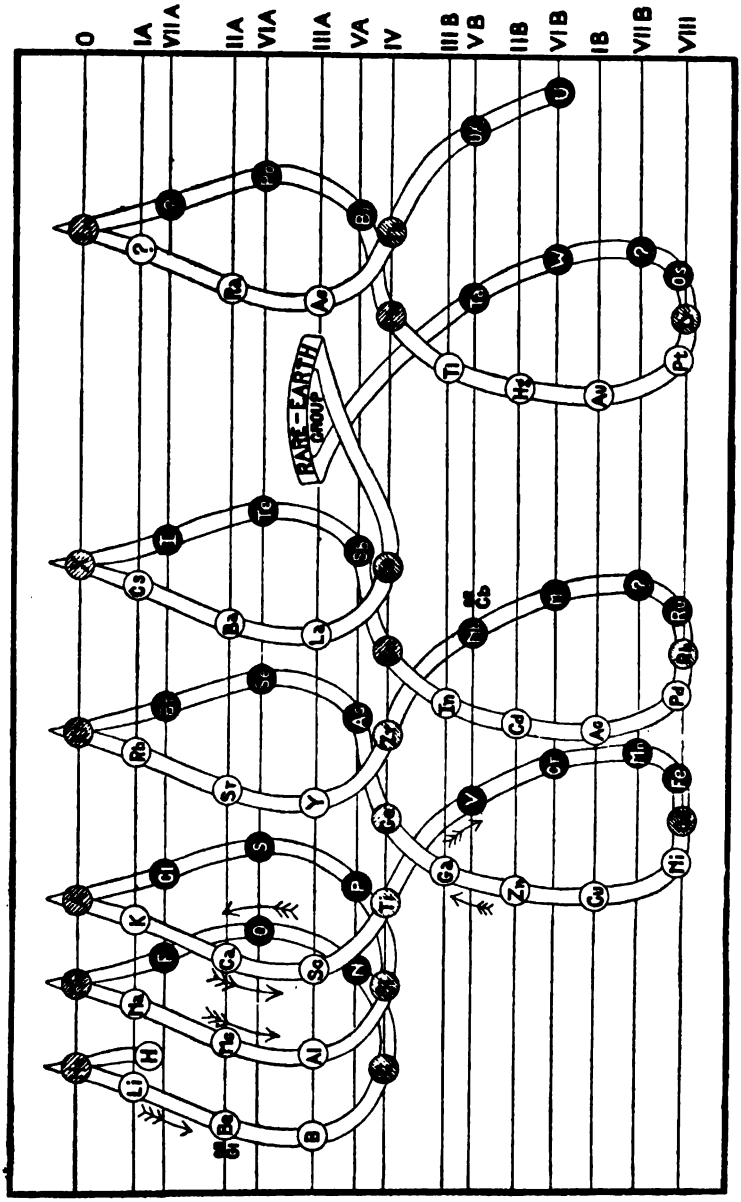
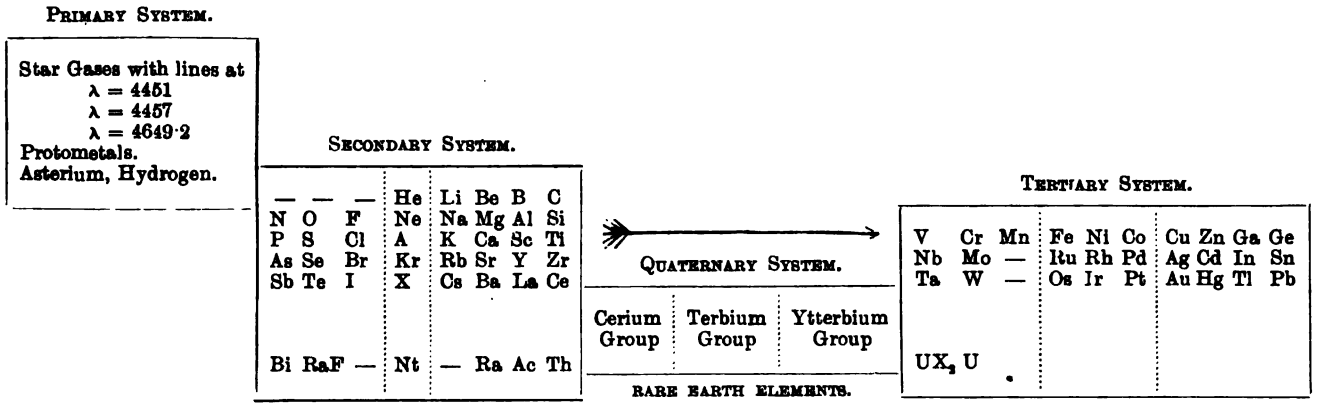


FIG. 87.

From Soddy's "The Chemistry of the Radio-Elements".

Digitized by Google


PRIMARY SYSTEM.
Star Gases with lines at
λ = 4451
λ = 4457
λ = 4649·2
Protometals.
Asterium, Hydrogen.
SECONDARY SYSTEM.
— — — He Li Be B C
N O F Ne Na Mg Al Si
P S Cl A K Ca Sc Ti
As Se Br Kr Rb Sr Y Zr
Sb Te I X Cs Ba La Ce
Bi RaF — Nt — Ra Ac Th
QUATERNARY SYSTEM.
Cerium Group
Terbium Group
Ytterbium Group
RARE EARTH ELEMENTS.
TERTIARY SYSTEM.
V Cr Mn Fe Ni Co Cu Zn Ga Ge
Nb Mo — Ru Rh Pd Ag Cd In Sn
Ta W — Os Ir Pt Au Hg Tl Pb
UX2 U

Digitized by Google

According to Schmidt, after the appearance of cerium, the evolutionary process progressed further in the same direction, so that there is a still closer approximation in properties among the elements of the rare earth group which forms his Quaternary System.

The dotted lines in the table bring out another point upon which Schmidt lays stress. In the centre of the Secondary System lie the inert elements, which form the transition from the electronegative to the electropositive series. Corresponding to this in the Tertiary System is the triad grouping of iron, cobalt and nickel, along with their congeners. Finally, in the Quaternary System, Schmidt regards the terbium group of elements as forming a bridge between the cerium and ytterbium groups; so that the general principle is observed throughout the arrangement.

The main defect of Schmidt's arrangement is that it throws no light upon the rare earth problem; for, as can be seen from the diagram, the ordinary sequence of the elements in the Secondary and Tertiary Systems continues normally even after the interposition of the Quaternary System.

Schmidt's arrangement has been given here, however, mainly in order to show that there are still fresh ways of regarding the Periodic Table; and it seems likely that in the future something better than our present system may be discovered.

7. *Surfaces Representing Periodic Properties.*

Two attempts have been made to represent the periodicity of elemental properties by means of surfaces. It is evident that any ordinary Periodic Table can be inscribed upon a plane surface, which leaves free the possibility of utilising a vertical co-ordinate to express a further property of the atoms.

Martin[1] constructs a periodic surface for each separate element in the following manner: Suppose the surface for sodium is required. The ordinary Mendeléef Table is plotted on a plane surface; and then from the centre of each space a perpendicular is raised the length of which is proportional to the affinity between sodium and the element corresponding to the space. The summits of all the perpendiculars are then united

[1] Martin, *Researches on the Affinities of the Elements.*

Digitized by Google

Univ. of California

Digitized by Google

(*a*). The Periodic Surface (front view).

(*b*) The Periodic Surface (side view).

FIG. 38. [*To face p.* 369.

Digitized by Google

to form a surface, which represents the relative magnitudes of the affinity of sodium for all the other elements. When affinity surfaces of all the elements have been prepared in this way, certain general characteristics are observed. For example, in the halogen group[1] it is found that all four surfaces have a kinship in form. In each case the highest points in the surface occur over the alkali metals and the affinity decreases rapidly both in the direction of high atomic weight or electronegative character (towards caesium or oxygen). The volume enclosed between surface and base diminishes on passing down the halogen group from fluorine to iodine. In the case of the last element, there is a marked increase in the altitude of the surface around oxygen, chlorine and bromine, owing to the amphoteric nature of iodine which is not exhibited by the lighter halogens to the same extent.

In Stewart's periodic surface,[2] the vertical co-ordinate is used to represent the atomic volume of the element; so that the surface gives a combined representation of the Periodic Table and the Atomic Volume Curve. Fig. 38 shows the model of the surface.

8. *The Possibility of a Wider Periodic Generalisation.*

The Periodic System has been examined and re-examined by so many minds that it now seems to have yielded us all the information to be derived from its present form; yet in spite of this, it still remains a mere empirical rule which suggests nothing with regard to underlying causes. Even the discovery of the connection between atomic numbers and the electrical constitution of the atom has failed to throw any clear light upon the periodicity in properties of the elements; for the analogies between atomic structure and the groupings of Meyer's floating magnets are not sufficiently close to be more than suggestive. If any advances are to be made in the study of elemental periodicity, it seems probable that they will come from a consideration of graphic rather than of tabular representations of the system; since a curve or a

[1] Illustrations of these are given in Friend's *Textbook of Inorganic Chemistry*, Vol. VIII., p. 17.

[2] Stewart, *Recent Advances in Physical and Inorganic Chemistry*, 1920, p. 251.

Digitized by Google

series of curves will often suggest relationships which are missed when the data are expressed in tabular form.

The pioneer in this field was Emerson Reynolds.[1] His views should be studied in the original papers; but the following summary of them will serve to bring out the main points upon which he touched.

The bases of his system are as follows: (1) He chose as the foundation of his arrangement the atomic weights. (2) In the earlier sections of the system the elements fall into sets of seven, of which the first three elements are electropositive, the fourth is transitional and the last three are electronegative. The elements Na, Mg, Al, Si, P, S, Cl illustrate this point. (3) In comparing period with period, the *alternate* members are those most closely related to each other. The meaning of this is made clearer if it be pointed out that Reynolds here refers to the resemblances between K, Rb and Cs on the one hand and between Cu, Ag and Au on the other. (4) There are two types of transition in the system, the one being marked by the argon group and the other by the cases like that of Mn, Fe, Co, Ni, Cu, where no abrupt change of electrochemical sign takes place in the series.

In order to express these facts graphically, Reynolds had recourse to the analogy of stationary waves in a knotted string, such as are set up when one end of a light cord is attached to a large tuning-fork kept in continual vibration. The diagram at the end of the volume gives Reynolds' symbolic representation of the elemental series. It will be noted that the elements in alternate periods are shown respectively as dots and crosses. Each knot in the cord is supposed to be travelling in a circular path at right angles to the axis of the whole system. The lengths of the loops in the cord increase up to the sixth loop and then decrease again, as would be the case were a uniform cord vibrating in a medium of unequal density or if the density of the cord were greatest at some point near the middle. An examination of the curve will show that the *adjacent* loops are in *opposite phases;* and, further, that this difference corresponds in the main to the difference between ascending and descending branches in the Atomic Volume Curve.

Reynolds next dealt with the members of the Eighth Group

[1] Reynolds, *Chem. News*, 1886, **54**, 1; *Trans.*, 1902, **81**, 612.

Digitized by Google

of the Periodic Table. These triplets, according to their atomic weights, should lie at nodes in the vibrating string; but in actual fact they cannot be so placed, since they exhibit chemical affinity. On this account Reynolds was led to suggest that they are members of a new series related harmonically to the first, somewhat as shown on the diagram by the larger loops, on which the triplets are indicated by dashes. They are thus *interperiodic* in a new sense of the word.

With regard to the position of hydrogen, Reynolds found that when a node was produced in the cord at a distance of four units from the vibrator—corresponding to the position of helium—the relation of loops and nodes was approximately that shown by the diagram; and this leaves an unfinished loop between helium and the vibrator. On this loop hydrogen finds its natural place as the last member of a pre-helium period.

Looking at the diagram as a whole, Reynolds drew attention to the following points. There are three types to be distinguished, to which he gave the names:—

Orthoperiodic.—The members of the twelve minor periods.

Macroperiodic.—The triplets about the antinodes of the greater periods.

Nodal.—The inert elements.

Broadly speaking, the scheme represents the atomic masses as forming part of a dual vibrating system, the two parts of which exhibit simple harmonic relations. Hydrogen is regarded as belonging to both series. In the nodal elements, helium also marks a point common to both systems. The occurrence of neon instead of a triplet series may be accounted for by the difference between the transition F-Na and the transitions Mn-Cu, Mo-Ag and ?-Au.

The assumption of macroperiodic vibration suffices to find a place for the triplets of the Eighth Group while still retaining them in the general bounds of the system. Reynolds, with careful reservations, suggested that the rare earth elements also belonged to the macroperiodic series.

It will be seen that Reynolds' views offer nothing in the nature of an "explanation" of the Periodic System; but they place the problem in a new light by the sifting out of the elements into three possible series with certain harmonic relations between them.

Digitized by Google

In view of recent advances in our knowledge, a second diagram has been placed alongside Reynolds' one; and it may not be without interest to point out the differences between the two. The atomic numbers have been chosen as a basis for the new diagram, as the atomic weights have ceased to be of fundamental importance in schemes of classification. Inspection of the diagram will show that it includes two short loops (each of which contains two tiny loops), two long loops, an extra long loop and a short loop. In some ways it is an improvement upon Reynolds' scheme, as it is more symmetrical in its arrangement of analogous elements: thus potassium, rubidium, and caesium appear at corresponding points on the orthoperiodic curve; the Eighth Group triplets also appear at equivalent positions on the macroperiodic line; and the rare earth elements are accorded a place on a new and wider loop. Carbon and silicon appear as members of the macroperiodic system; whilst beryllium and magnesium obtain places which differentiate them from both zinc and calcium. The general sequence of the elemental order is shown by the heavy lines running through the diagram. It will be seen that this regrouping of the elements provides for the renewal of the ordinary periodicity after niton.

Digitized by Google

CHAPTER XX.

SOME VIEWS OF ATOMIC STRUCTURE.

1. *Introductory.*

LOOKING back over men's ideas of the constitution of matter, it is impossible not to be struck by the fact that throughout the history of the subject there has been a series of oscillations between two diametrically opposed fundamental views. On the one hand, a school has taught that behind all the differences in properties there is homogeneity; so that matter in its multitudinous forms is actually built up from some material which is common to all substances: and the opposing school has always maintained that at the root of things there lie more than one elemental material, so that matter cannot be reduced to a unitary form.

In the very earliest speculations on the elements, earth, air, fire and water were regarded as the four foundation-stones of the universe: so that evidently the authors of this view took heterogeneity as their basis. Then came the alchemistical period, in which the idea of homogeneity appears to have gained the upper hand; for unless the elements had some common substratum, it is difficult to see how the transmutation of lead into gold could have been deemed possible. With the dawn of true chemistry and the exacter examination of chemical processes, the doctrine of heterogeneity took a fresh lease of life. The isolation of a larger number of elements, coupled with the determination of chemical equivalents made it seem doubtful if the idea of homogeneity could be maintained. Nevertheless, with the propounding of Prout's hypothesis, the old doctrine reappeared once more to fascinate many by its simplicity; but again it fell into disfavour as a knowledge of exact atomic weights increased. At the beginning of the twentieth century, however, the inter-relation between the

Digitized by Google

forms of matter which we term elements was thrown into a new light by the discoveries in radioactivity. The disintegration of radium into helium and niton proved conclusively that the elements were not necessarily independent of each other; for there was evidently a genetic relationship traceable between some of them; and the conversion of one element into another was definitely established. Further, from the same branch of research came the proof that electricity was intimately associated with the atom.

In the field of energy, somewhat similar processes of evolution had occurred. The idea of discontinuity was involved when heat, light, magnetism and electricity were all regarded as different properties of matter. Then, step by step, came the recognition of the identity of heat and light, of the relations between magnetism and electricity; until the coping-stone was set in place by Clerk Maxwell's electromagnetic theory of light. Again, in the older view, radiation was assumed to be a continuous process; whereas in more modern times Planck's hypothesis has been accepted in many circles and the idea of a discontinuous mode of radiation has been found to solve certain problems which previously had offered difficulty.

In the present chapter, the main concern is with matter; and it may be well to refer briefly to some of the older ideas of atomic structure before dealing with more recent views upon the subject. It must be remembered that in pre-radioactivity days, the fundamental problem before the constructor of model atoms was to provide a system which would be perpetually stable. This Kelvin attempted to do in his hypothesis of vortex-atoms. By assuming the formation of vortices in a frictionless ether, he was able to attain the indestructible machine which the atom then appeared to be; and on his view matter was simply a series of vortex-rings produced in an ethereal medium. From the purely chemical standpoint, it must be admitted, this hypothesis was of very little assistance; and with the discovery of radioactive disintegration it seems to have lost its value even upon the physical side.

The same may be said of the ether-squirt hypothesis of Karl Pearson.[1] In Pearson's view, matter is merely a swiftly flowing current of ether. Just as the jet of a fire-hose, though

[1] Pearson, *The Grammar of Science.*

Digitized by Google

composed of a liquid, has some of the properties of a solid—it behaves like a solid when struck—so Pearson assumed that a jet of ether travelling at high velocity would take on the semblance of matter; and he suggested that from outside the known Universe ether was being poured out under high pressure through a series of "squirts" and removed through a series of "sinks". Each "squirt" and "sink" would represent what we term matter. Here again, it will be seen, the chemist gets but little help in the problems which confront him

Another suggestion was made by Osborne Reynolds,[1] which goes by the name of the "dilatancy" theory of matter. Reynolds boldly inverted the ordinary relations of matter and ether and regarded the former as being a series of pores or holes in an immensely solid ethereal medium. Here also, there is little that chemistry can utilise to solve its difficulties.

Finally come the modern electrical theories of matter with which the following sections will deal. But before entering upon the discussion of them, something must be said with regard to the general question. It cannot be too strongly emphasised that at the present day the problem of atomic structure is being approached from two different directions, the physical side and the chemical aspect. The physicist is concerned entirely with the physical properties of matter such as spectra, electrical behaviour, etc. He has no concern with and takes little interest in the chemical properties which matter exhibits. The result of this is that the model atoms devised by physicists are not directly applicable to chemical problems, though they are of chemical interest to some extent. Again, the physical model atom is generally constructed with a view to harmonising with certain quantitative experimental results, whether these be obtained in the field of radiation or in branches concerned with electrical properties; and it has thus taken on a mathematical aspect. On the chemical side, however, these quantitative measurements are still lacking to a great extent; and therefore the chemist's model atom is very much less amenable to quantitative treatment. Further, since a true "chemical" model atom is first and foremost concerned with chemical properties, which are not yet standardised, it is rather absurd

[1] Osborne Reynolds, *Collected Scientific Papers.*

Digitized by Google

to demand that such a "chemical" atom should yield quantitative mathematical results like the "physical" model atom which is designed specially to concord with purely physical measurements. Those who imagine that the chemical model atom is inferior to the physical model, because it cannot be handled mathematically at this stage, might ask themselves with some profit whether the physical atom has thrown very much light upon our chemical problems; or whether it is not actually the fact that when the physical atom is tested by chemical phenomena it fails just as conclusively as the chemical atom does when it is transferred to the physical arena.

The truth is that each type of model atom is devised to suit certain parts of the whole subject; and that we are at present unable to suggest any model which will fulfil both the physical and the chemical demands simultaneously. It is no discredit to the physical atom that it fails in the chemical field; nor is it to be wondered at if the chemical model breaks down on the physical side. We are probably still far from the point at which the two branches will flow together; and from the chemist's point of view, the chemical model atom is the more promising of the two, since it at least attempts to deal with the problems which confront him.

2. *Some Points in our Knowledge of Atomic Structure.*

Before entering upon a discussion of the model atom, it may be well to collect together the main pieces of information which have been acquired with regard to atomic structure in general; and this may most conveniently be done by propounding a set of questions and giving the answers to them which are suggested by research.

1. *Is the atom purely material in nature or does it contain electricity?*—In the case of the radio-elements, electrical charges are spontaneously ejected from the atomic system during disintegration processes; and this seems to establish definitely that atoms are built up in part at least from electrons. Since normally the atoms of the elements are electrically neutral, it is evident that the positive and negative charges in them are equally balanced.

2. *Is the negative electricity in the atom uniformly distributed through the atomic system or are there two or more*

Digitized by Google

main concentrations of it in the atomic structure?—When a radio-element ejects a negative electron in the form of a β-ray, the valency of the element becomes increased by one unit. The same increase of one unit is observed when an ion undergoes oxidation, as in the passage from ferrous iron to ferric iron; and thus the question above corresponds to the inquiry whether or not the electron of the β-ray change comes from the same part of the atomic structure as the electron which is displaced in valency changes occurring in ordinary chemical reactions. At the suggestion of Soddy, this point was investigated by Fleck,[1] who established conclusively that the point of origin of the β-ray electrons was not the same as that at which the valency electrons originated.

Fleck's investigations were based upon the following reasoning. By a sequence of two β-ray changes involving the loss of two electrons, the quadrivalent element uranium-X_1 is converted into the hexavalent element uranium-2. A parallel to this is furnished by the conversion of a quadrivalent uranous ion into a hexavalent uranyl ion. In both cases, the material gains two positive charges as the net result of the process. Now uranium-2 is isotopic with uranium-1 (ordinary uranium); and is therefore chemically inseparable from the latter. Therefore, if the β-ray change and the ionic change are similar in nature, the two starting substances also should be isotopic with each other and inseparable by chemical methods. In other words, a uranous salt and a salt of uranium-X_1 ought to be chemically inseparable.

Quadrivalent.		Isotopic. Hexavalent.
UX_1	β-ray change →	U-2
U^{IV}	Ionic change →	U-1
Th		

It was not necessary to examine uranium-X_1 itself, since any of the isotopic elements of this set would do as well. Fleck chose thorium as the test substance; and he was able to show that although thorium and uranous uranium are very closely akin chemically, they are none the less separable from each other. This proves that they are not isotopic; and that therefore quadrivalent uranium and uranium-X_1 are not isotopic

[1] Fleck, *Trans.*, 1914, **100**, 247.

Digitized by Google

with each other: from which it follows that the changes resulting from β-ray emission and ionic variation are not identical processes. But since the *electrons* are identical in both cases, the only difference between the two processes must lie in the points of origin of these electrons—which established the fact that there are two different groups of negative electrons in the atom. One of these contains the electrons taking part in ionic changes; the other group emits the electrons which form β-rays.

3. *Is the positive charge of the atom concentrated in one spot or is it distributed uniformly throughout the system?*—This question finds its answer in the results of some experiments upon the scattering of α-particles by metallic atoms.[1] When a stream of α-particles is allowed to pass through a thin sheet of metal, it is found that some of them are stopped entirely or are deflected from their original paths. This phenomenon is termed *scattering*. Calculation establishes the chance of the particles passing through the interstices between the molecules of the metal; and from the results of experiments it must be inferred that these charged helium atoms in many cases actually traverse the atoms of which the metal sheet is composed. The deflections must therefore be regarded as being produced, not by atomic collisions, but by the action of electrical charges within the atomic structure.

Now, from the magnitude of the deviations observed, it is clear that a strong force is at work; and this force can hardly be supposed to reside in the negative electrons; since their mass is only about one seven-thousandth of that of a helium atom and if any measurable deviation took place it would probably be that of the negative electron by the α-particle and not *vice versâ*. It was therefore assumed by Rutherford that the deflection of the α-particle was due to the repulsive action of a large positive charge situated at the centre of the atom, as shown in Fig. 39. Here it will be seen that (I), the deflection of the particle by the negative electrons is slight, whereas (II), the positive nucleus of the atom exerts a very powerful effect.

This hypothesis of a central positive nucleus has been found to be in agreement with the results of experiment; and calculations made from observations on gold sheets go to prove that

[1] See Rutherford, *Radioactive Substances*, 1913, pp. 180, 618.

Digitized by Google

the number of positive charges in the nucleus of the gold atom is about half the atomic weight and is equal to the atomic number of the element which acts as a scattering medium. According to Rutherford's views, the whole mass and the positive charges of the atom are concentrated within a sphere of radius not greater than 10^{-12} cms.

4. *Is there any relation between the number of positive charges in the atomic nucleus and the atomic number of the element?*—As has just been pointed out, the atomic number appears to be equal to the number of positive charges grouped together in the atomic nucleus. When an atom loses two positive charges on the ejection of an α-particle, its atomic number is reduced by 2.

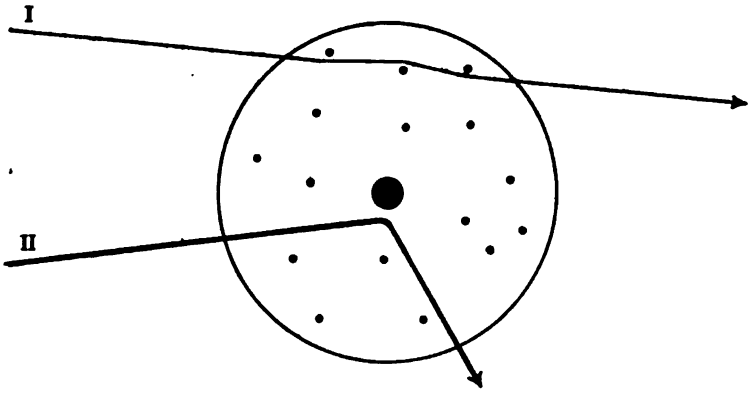


FIG. 89.

5. *Are there any traceable differences between positive and negative electricity with respect to matter?*—Negative electrons are known to exist apart altogether from matter—*e.g.*, in the cathode rays—but positive charges have never been detected except in presence of matter. It seems clear that mass and positive electricity are closely related to one another.

6. *Is there any permanent connection between the positive and negative charges within the atom?*—Apparently the positive and negative charges can act entirely independently of each other; for in the radio-elements it has been found that disintegration may take place by: (1) the ejection of two positive

Digitized by Google

charges with the α-particle; or (2) by the loss of a negative electron in the β-ray; or (3) the same element may disintegrate simultaneously in two different ways, losing an α-particle in the one mode and a β-electron in the other. No case is known in which an atom parts simultaneously with positive and negative charge.

7. *Apart from their points of origin, is there any difference between the electrons involved in ionic changes and those ejected during β-ray disintegration?*—It is obvious that there is a profound difference between these two, since the "ionic" electrons are readily removed from or replaced in position by ordinary chemical action, whereas the electrons of the β-rays are spontaneously and uncontrollably driven out of the atom and cannot be brought back to their point of origin by any forces at our disposal. Further, the ejection of a β-ray electron causes a change in the atomic number, whereas the loss of an "ionic" electron, though it produces a change in chemical properties very similar to that involved in the loss of a β-ray, is not quite so definite in its effects and it produces no alteration of the atomic number.

8. *Is the atomic weight the governing factor in elemental character?*—Since several elements are known which have different atomic weights and which are yet chemically inseparable, it is evident that the atomic weight and the chemical properties of atoms are not interdependent. This is confirmed by the fact that certain elements having identical atomic weights show totally different chemical properties.

9. *Is there any connection between spectra and atomic structure?*—The facts given in a previous chapter show that there is a simple relation between the frequencies of some of the X-ray spectral lines and the atomic numbers; and there is a kinship between the spectra of elements of the same family which also appears to be related to atomic architecture.

The facts mentioned in the foregoing paragraphs show how complex a problem presents itself to the designers of model atoms; and it is almost unnecessary to say that no perfect model has yet been suggested. In the following sections a description will be given of several attempts which have been made to attack the problem; but the reader should bear in mind in each case how very partial is the success achieved.

Digitized by Google

3. *Drawbacks of a Saturnian Atom.*

By a Saturnian atom is meant one in which negative electrons revolve in orbits around a central positive nucleus, just as the bodies making up Saturn's rings revolve around the planet. When this conception is applied to atomic structure, it is almost self-evident that two difficulties are immediately encountered.

In the first place, Rutherford has shown experimentally that the positive nucleus of the gold atom, for instance, contains some seventy-nine positive charges so closely associated that they all lie within a sphere with a radius of 10^{-12} cms. Now, under ordinary conditions, two positive charges repel each other; so that the cohesion of these seventy-nine charges is not compatible with well-known phenomena. It is clear, therefore, that in order to conceive the existence of Rutherford's nucleus, we must be prepared to make the assumption that at extremely small distances, two similar charges do not repel each other but actually tend to draw together. There is, of course, another hypothesis which would serve the purpose. Since mass and positive electricity are apparently associated, it seems probable that the whole mass of the atom is concentrated in the tiny nucleus; and this would imply that the material of the nucleus was of enormous density, far exceeding anything with which we are acquainted. With this enormous concentration of mass in the positive electrons and with very small distances between the particles, it is clear that the gravitational forces in the system would be greater by far than anything known outside the atomic world; and it might be assumed that these gravitational attractions were sufficient to hold the particles of the nucleus together in spite of the repulsive forces between the positive charges. This matter, however, is one of pure speculation at present.

The second difficulty involved in the Saturnian conception of the atom lies in the fact that any such model atom would radiate energy continuously and would thus eventually "run down". Not only so, but since an atom of this type would be losing energy uniformly, it would radiate a continuous spectrum. Here the Saturnian idea, in its simplest form, is in direct conflict with experimental evidence. Hydrogen,

Digitized by Google

for example, does not radiate a continuous spectrum at all times. It emits a spectrum only when it is ionised by an electric current; and this spectrum, when emitted, is not a continuous one but is a discontinuous line spectrum in which, as has been pointed out in a previous chapter, the frequencies of the lines are related to one another in agreement with the expression—

$$\nu = N\left(\frac{1}{n_1^2} - \frac{1}{n_2^2}\right)$$

in which ν = frequency, N = constant, $n_1 = 2$ for all lines in the visible spectrum and n_2 is successively 3, 4, 5, 6. . . .

From these facts it is clear that in order to make the Saturnian form of atom fit the case it must be considerably modified by further postulates, so as to evade the difficulties which beset it in its simplest guise.

4. *Bohr's Atom.*

A model atom which has attracted a considerable amount of attention was suggested by Bohr.[1] It was originally devised to deal with the case of a single electron revolving around a positive nucleus—the case of the hydrogen atom—but it has been applied to more complex systems also, though the results in this case are by no means so successful.

Bohr makes three assumptions:—

1. If an electron rotates around the nucleus of an atom, it may do so not in one fixed orbit, but successively in several different orbits, springing from one orbit to the other from time to time.

2. No radiation occurs while the electron is confined to one orbit; but when it jumps into a fresh orbit, then radiation takes place during the transition.

3. The various possible circular orbits of an electron must fulfil certain conditions.

It must be pointed out that Bohr's atom depends upon a fusion of Newtonian dynamics with the quantum theory of Planck, which certainly appears a curious mixture. However, it may be well to show briefly how this fusion works; and

[1] Bohr, *Phil. Mag.*, 1913, **26**, 1, 476, 857; 1915, **29**, 332; 1915, **30**, 394.

Digitized by Google

this can best be done by taking each of the assumptions in turn.[1]

1. In each of its possible orbits, the rotating electron is assumed to be governed by the ordinary Newtonian law, which in this case takes the form—

$$\frac{eE}{a^2} = (2\pi n)^2 ma \quad . \quad . \quad . \quad . \quad (1)$$

where e = the charge on the electron; E = the charge on the nucleus; a = the radius of the orbit; n = the orbital frequency; and m = the mass of the electron.

2. Radiation occurs only when the electron jumps from one orbit to another. If A_1 represents the energy of the electron in one orbit and A_2 represents its energy in a second orbit, then obviously the amount of energy radiated is $A_1 - A_2$. Now this energy must be radiated at a certain frequency, say ν; and Bohr, introducing Planck's constant, h, obtains the following expression:—

$$h\nu = A_1 - A_2 \quad . \quad . \quad . \quad . \quad (2)$$

3. The limitations mentioned in the third assumption are arrived at in the following way: Bohr assumes that the various possible circular orbits of the electron are determined by assigning to each orbit a kinetic energy T such that—

$$T = \tfrac{1}{2}\tau hn \quad . \quad . \quad . \quad . \quad (3)$$

in which τ is an integer, n is the orbital frequency and h is Planck's constant. The value of T is chosen so as to make a series of frequencies agreeing with that which is actually observed in the hydrogen spectrum (the Balmer series).

Now, in order to test the validity of Bohr's conception, the value of the constant N may be calculated from his assumptions and the result compared with the value of N obtained experimentally. The calculation is a simple one. We have, from Bohr's first assumption, equation (1)—

$$\frac{eE}{a^2} = (2\pi n)^2 . ma \quad . \quad . \quad . \quad . \quad (1)$$

[1] Millikan's treatment of the question (*The Electron*, Chapter IX.) has been utilised here, as it presents the matter in its simplest form.

Digitized by Google

Now, the kinetic energy of the rotating electron is $\frac{1}{2}m(2\pi na)^2$; and from (1) we obtain the equality—

$$\tfrac{1}{2}m(2\pi na)^2 = \tfrac{1}{2}\frac{eE}{a}$$

The work required to move the electron from its orbit to a position of rest at infinity is given by—

$$\frac{eE}{a} - \tfrac{1}{2}m(2\pi na)^2 = \tfrac{1}{2}\frac{eE}{a}$$

If this value be called T, then—

$$2a = \frac{eE}{T} \text{ and } n = \frac{T^{\frac{1}{2}}\sqrt{2}}{\pi eE\sqrt{m}}$$

Combining this result with Bohr's third assumption that $T = \frac{1}{2}\tau h n$ we obtain the expressions—

$$T = \frac{2\pi^2 me^2E^2}{\tau^2h^2} \quad 2a = \frac{\tau^2h^2}{2\pi^2meE} \quad n = \frac{4\pi^2me^2E^2}{\tau^3h^3}$$

Now, during a change of orbit, energy is radiated which can be expressed thus—

$$T_{\tau_1} - T_{\tau_2} = \frac{2\pi^2me^2E^2}{h^2}\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

Putting this as equivalent to $h\nu$, we obtain—

$$\nu = N\left(\frac{1}{\tau_1^2} - \frac{1}{\tau_2^2}\right)$$

where

$$N = \frac{2\pi^2e^2E^2m}{h^3}$$

In the case of hydrogen, since there is one negative charge and one equal positive charge, $e = E$; and the expression simplifies to—

$$N = \frac{2\pi^2me^4}{h^3}$$

This equation gives the calculated value of N expressed in terms of e, m and h. Millikan[1] has determined the value of e to be 4774×10^{-10}; and his determination[2] and that of Webster[3] for Planck's constant give a mean figure $6{\cdot}545 \times 10^{-27}$

[1] Millikan, *Proc. Nat. Acad.*, April, 1917.
[2] Millikan, *The Electron*, 1921, p. 227.
[3] Webster, *Phys. Rev.*, 1916, 7, 599.

Digitized by Google

Bucherer has found that e/m has the value $1{\cdot}767 \times 10^7$. Using these figures in the equation above, the calculated value of N is found to be $3{\cdot}294 \times 10^{15}$; whilst the value actually observed by experiment is $3{\cdot}29 \times 10^{15}$. The agreement between practice and the Bohr theoretical value is within 0·1 per cent.; which certainly provides striking support to Bohr's ideas.

When various integral values are assigned to τ_2 and putting $\tau_1 = 1$ it is possible to calculate the frequencies of the various lines in the hydrogen spectrum with great accuracy.

The foregoing will suffice to give some idea of the Bohr model atom and the reasoning upon which it is founded. Clearly it gives remarkably good results in the case of the hydrogen spectrum; but in the case of more complex systems such as helium and lithium, it does not fare quite so well.

On the purely chemical side, however, with which we are mainly concerned, it is almost valueless; for it throws no light whatever upon our particular problems, apart from spectroscopic affairs. It leaves the field of radioactive change quite unilluminated; and in ordinary chemical reactions it fails to help us at all. Indeed, if Bohr's ideas be applied to certain chemical questions, they seem to lead on to inferences which are not in accordance with facts. For example, Bohr regards radiation as being produced by the "jump" of an electron from one orbit to another during ionisation; but no radiation phenomena have been observed in the case of the ionisation of acids in solution, though here the electronic "jump" is so great that it actually ends in the complete removal of the electron of the hydrogen atom outside the atomic system altogether. Similarly, when a hydrogen ion touches the electrode and picks up an electron, one would expect to find that as this electron settled down in the atomic structure it would give rise to radiation; for it can hardly be supposed that it immediately sinks into a stable orbit. Yet no such radiation seems to have been observed.

The Bohr atom, then, is of physical but hardly of chemical interest at the present time; and it seems unlikely to throw much light upon the matters which are important to the chemist.

Digitized by Google

5. *Nicholson's Atom.*

The model atom of Nicholson[1] differs from that of Bohr in that it demands only the classical mechanics and does not require the application of the quantum theory. It would occupy too much space if Nicholson's calculations were given; and it will be best to confine the treatment to a summary of the main ideas involved in his conception. In the first place, he differs entirely from Bohr in his views on the origin of the energy which appears as radiation. Bohr assumes this to arise through a gradual settling down of the rotating electrons of the atom into a series of orbits, the settling-down process being accompanied by the radiation of energy. Nicholson, on the other hand, regards radiation as being the result of external forces acting upon the atom and producing changes in the motions of its component electrons.

In the Nicholson atom, the electrons are conceived as rotating steadily in a ring about the nucleus. The influence of external forces then tends to make them undergo a fresh type of vibration, this time perpendicular to the plane of the ring. This hypothesis obviously entails the conclusion that the character of the vibrating system depends upon the number of electrons in the ring. For example, the ring may vibrate as a whole, always remaining parallel to its original position; or it may vibrate in halves, so that two nodes and two crests travel round the ring. On these assumptions, Nicholson was able to calculate the ratios of the wave-lengths of a series of lines in a spectrum and thus, by assuming the wave-length of one particular member of the series he was able to predict the wave-length of the remaining lines in the series.

When the results calculated by Nicholson were tested by comparison with observed results, a most surprising series of successes came to be recorded. For example, the element nebulium is known only through the fact that lines ascribed to it occur in the spectra of certain nebulæ. Nicholson applied his theory to this case and was able to show that he could account for all the lines except two, which did not fit in with his work. At that time, Wolf was engaged in the examination of nebular spectra; and he observed that in the case of the ring nebula of

[1] Nicholson, *Month. Not. Roy. Astron. Soc.*, 1911, **72**, 49, 139, 677, 729; 1912, **73**, 382; 1913, **74**, 204, 425, 486, 623.

Digitized by Google

Lyra some of the nebulium lines are emitted by the interior of the nebula, others by its exterior, which shows that the so-called "nebulium spectrum" is really a composite of two spectra. More wonderful still, the two lines which Nicholson found to be anomalous are the very lines which are thus shown to be alien to the true nebulium spectrum. This furnishes an extraordinary support to the Nicholson theory.

Again, Nicholson, from his calculations, predicted the occurrence in the nebulium spectrum of a line at wave-length 4352·9, which had not been observed up to that time. An examination of the old plates of the Lick Observatory showed that there was actually a line at this point, though it was so faint that it had escaped notice until attention was specifically drawn to its position.

Still further, Nicholson has been able to show that his system agrees with twenty-one out of twenty-seven lines in the spectrum of the solar corona; and he has applied it also to the case of the Wolf-Rayet stars, which are supposed to represent the primary stage of stellar evolution. He has been able to calculate the probable atomic weights of materials which on his theory lie between hydrogen and helium in the elemental series in the following manner:—

He assumes that the mass of an atom (as determined by its inertia) must be equal to the sum of the inertias of all its positive and negative charges; and since the mass of the negative charges is very slight, they may be omitted from the calculation.

Let r = radius of the positive nucleus of the atom and let e = charge on an electron. If there are n electrons in the neutral atom, there must obviously be n positive charges present; and the total charge on the nucleus will be ne. The inertia of the nucleus (and therefore of the whole atom) will thus be n^2e^2/r.

Now assume that the positive charge is uniformly distributed throughout the volume of the nucleus. Since this volume varies with ne, we have

$$\tfrac{4}{3}\pi r^3 = \mathrm{K}en$$

and since π and e are constants, this becomes $r^3 = \mathrm{K}n$ or $r = \mathrm{K}n^{\frac{1}{3}}$.

Substitute this value of r in the expression n^2e^2/r and we obtain:—

$$\text{Inertia of nucleus } \frac{n^2e^2}{\mathrm{K}\sqrt[3]{n}} = \mathrm{K}\sqrt[3]{n^5}.$$

Digitized by Google

Hence the inertia—which can be regarded as a measure of the atomic weight—is proportional to n where n is the number of negative charges in the atom.

Now Nicholson assumes that hydrogen contains in its system three negative and three positive charges, which leaves systems of 2, 4 and 5 charges to represent other elements. Taking the value of n in each case, Nicholson obtained a series of numbers which give the ratios between the atomic weights of the various elements; and since the atomic weight of hydrogen is 1·008, the atomic weights of the remainder can be calculated by simple proportion:—

n.	Element.	$\frac{2}{5}\sqrt{n^5}$.	Atomic Weight.
2	Coronium . .	3·1748	0·51282
3	Hydrogen . .	6·2403	1·008
4	Nebulium . .	10·079	1·6281
5	Protofluorine . .	14·620	2·3615

On the basis of these hypothetical atomic weights, Nicholson then made a further advance; though it is doubtful whether his results in this new field can claim the same importance as his previous ones. He regards the atoms of the more complex elements as containing as constituents the atoms of lighter elements. For example, the helium atom he assumes to be built up from one atom of nebulium and one atom of protofluorine; whilst neon is composed of six protofluorine atoms plus six hydrogen atoms:—

Nebulium	1·6281	6 Hydrogen	6·048
Protofluorine . . .	2·3615	6 Protofluorine . . .	14·169
	3·9896		20·217
Atomic weight of helium = 3·99		Atomic weight of neon = 20·21	

In view of the work of Aston[1] on mass-spectra, however, it seems doubtful whether such attempts at atomic architecture can be regarded as satisfactory at the present time. For example, Aston has shown that isotopic with neon there is another gas meta-neon with an atomic weight 22. If this be supposed to be built up like neon, it must contain two extra hydrogen nuclei or possibly an extra nebulium nucleus; but the

[1] Aston, *Nature*, 1919, **104**, 393; 1920, **105**, 8; *Phil. Mag.*, 1920, **39**, 449.

Digitized by Google

atomic architecture certainly gives us no clue to the identity of the two materials as far as chemistry goes.

Harkins and Wilson[1] have attempted to produce an atomic architecture on Nicholson's lines; but their method results in the conception that both argon and calcium are built up from ten helium atoms, while no satisfactory explanation is given of the total chemical dissimilarity between the two systems.

It seems probable that at the present stage of our knowledge we can do little to throw light upon atomic architecture; and we must wait for further developments in this field.

6. *The Lewis-Langmuir Atom.*

In the foregoing sections, the two most successful physical model atoms have been described; and it cannot have escaped the reader that, though they are interesting from the spectroscopic standpoint, their possible application to the problems of pure chemistry is practically negligible. They throw no light upon the fundamental questions with which chemistry is concerned; and in the field of valency especially they appear to be incapable of yielding anything whatever.

It seems therefore desirable to turn to the suggestions of chemists with regard to atomic structure and to see whether more light can be gained in this way. The chemical model atom, being devised to account for a set of phenomena of much wider scope than the physical model, is naturally at present in a more or less tentative stage; and to demand quantitative spectral results from it is to misunderstand the state of affairs. Our model atoms must be judged entirely from the chemical standpoint; and if they are successful in accounting for the phenomena of chemical relationships and reactions, they have fulfilled the object in view of which they were devised.

Now upon this basis, it is evident that there are two possible modes of procedure. The model atom may be regarded as a static system or as a dynamic arrangement of electrons. It will be simplest to take up the static idea in the first place and to deal later with the dynamic suggestions which have been proposed.

The most successful statical atom was suggested by G. N.

[1] Harkins and Wilson, *J. Amer. Chem. Soc.*, 1915, **37**, 1383.

Digitized by Google

Lewis[1] and elaborated by Langmuir.[2] As Langmuir's paper would lose so much by condensation, it will be best to confine attention to Lewis' views and to refer the reader to Langmuir's original paper for further information.

According to G. N. Lewis, every atom contains a kernel and a shell. The kernel is uninfluenced by ordinary chemical changes and possesses an excess of positive charges equal in number to the ordinal number of the group in the Periodic Table to which the element belongs. The number of negative electrons in the shell may vary on account of chemical changes between 0 and 8. The atom tends to retain in its shell an even number of electrons and especially to hold eight electrons, which are assumed normally to be situated at the corners of an imaginary cube.

It is assumed by Lewis that the atomic shells of two atoms are mutually interpenetrable and that electrons may pass readily from one position of the shell to another. The crux of the hypothesis lies in the assumption that one electron may occupy simultaneously the corners of two cubes if they be brought into superposition. By a further superposition, two pairs of corners may be superposed on one another and thus a second electron will become common to both systems. In this way single and double bonds are represented.

As Lewis shows, his model permits a distinction between certain types of bonds; and differences in reactivity are thus expressed. Finally, if it be assumed that the electrons in the shell are free to move along the edges of the cube toward the middle of the edge, an electronic grouping is obtained which corresponds to the van't Hoff-Le Bel tetrahedric arrangement about the carbon atom.

From the foregoing, it will be seen that Lewis depicts the valency side of the atom as a static arrangement in which the valency electrons are grouped in fixed positions around the nucleus. The main drawback of such a conception is that it fails to account for the influence of a change of valency upon the absorption spectra of compounds. For instance, the ferrous iron is green whilst the ferric ion has a deep yellow tint; and since absorption spectra are produced by the absorption of

[1] G. N. Lewis, *J. Amer. Chem. Soc.*, 1916, **38**, 762; *Science*, 1917, **46**, 297.
[2] Langmuir, *J. Amer. Chem. Soc.*, 1919, **41**, 1543; 1920, **42**, 274.

Digitized by Google

vibrations of certain periodicities, it is clear that the mode of vibration in the ferrous ion must be different from that of the ferric ion, since they absorb light of different wave-lengths. This seems to necessitate the idea that the valency electrons are not absolutely static but have certain definite vibration-periods. Thus Lewis' model, in order to be brought into conformity with our knowledge, requires the further assumption that the valency electrons of the shell are not fixed but are vibrating about mean positions and that the frequency of this vibration alters when one or more electrons are removed from the system. If this modification were introduced, it seems possible that Lewis' atom might help us toward an explanation of the work of Crymble upon the absorption spectra of ions.[1]

Langmuir's development of the Lewis' atom is based upon three main assumptions: (1) The electrons round the nucleus are arranged in successive sheaths with the following numbers in each: 2, 8, 8, 18, 18 and 32, corresponding to the periods of the table. (2) Two atoms may be coupled together by one or more duplets held in common by the completed sheath of the atoms. (3) The residual charge on each atom or group of atoms tends to a minimum.

7. *Noyes' Atom.*

Passing from the static conception of the atom to dynamic systems, the model atom proposed by Noyes[2] is the first which need be described. He assumes that atoms are built up from two sets of negative electrons: (1) those attached permanently to the positive nucleus and (2) those which are free to wander from atom to atom. When two atoms capable of chemical union are brought into close proximity, Noyes suggests that a valency electron rotating around the positive nucleus of the first atom may find the positive nucleus of the second atom so close to it that it falls under the simultaneous influence of both positive nuclei and proceeds to describe a new orbit around the two centres. This orbit will lie within the sphere of action of both positive nuclei and in one portion of its path the electron will pass within the confines of the first atom, whilst further on it will enter the boundary of the second atom. As a result of this, there will be a steady alternation of electrical character in both atoms, for

[1] See p. 37. [2] Noyes, *J. Amer. Chem. Soc.*, 1917, **39**, 879.

Digitized by Google

when the electron leaves its original atom and passes into the second atom, the latter will become negatively charged whilst the first atom will acquire a positive charge. A return of the electron along its orbit into the first atom results in electrical neutrality; and during this period the two atoms might fall apart, since they are no longer attracted toward each other. When ionisation occurs, Noyes assumes that the electron permanently leaves the first atomic system and revolves exclusively about the positive nucleus of the second atom. In this way the original atom acquires a permanent positive charge and becomes a cation, whilst the second atom, in virtue of its extra electron, is negatively charged and acts as an anion. If it be assumed that there are four or eight positive nuclei in the carbon atom, Noyes' hypothesis serves to account for the tetrahedral grouping found in optically active carbon compounds.

The most interesting and suggestive application of Noyes' hypothesis is to be found in the case of monomolecular reactions.

It is not too much to say that when our knowledge of this field has been perfected, we shall be on the edge of understanding the mechanism of all chemical reactions. The point is worth developing in some detail, since it is usually passed over very lightly in most works.

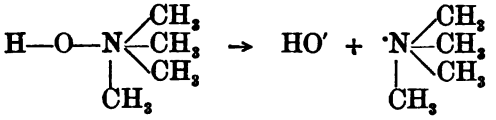
In a monomolecular reaction, whether it be one of intramolecular rearrangement or of decomposition, a certain fixed proportion of the material undergoes change in a fixed time. This can be accounted for only by the assumption that each molecule passes periodically through a condition of instability, during which it is liable to break up entirely (as in a decomposition reaction) or to break up and reform again into a new structure (as in intramolecular change). On this assumption, the velocity constant of a monomolecular reaction is a measure of the frequency with which the molecule passes through this state of instability. Thus, in order to produce a satisfactory hypothesis accounting for monomolecular reactions, it is necessary to devise an atomic mechanism which will pass periodically through an unstable equilibrium. If such a mechanism can be devised, it will serve to account for all chemical reactions; for in the case of the polymolecular reactions it is only necessary to assume that all the molecules involved have their particular unstable periods and that action

Digitized by Google

between them occurs when two or more molecules simultaneously attain the state of instability and collapse; after which their component parts will attract whatever atoms yield the stablest system; and in this way new compounds will be formed.

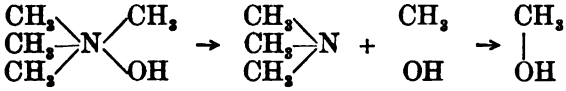
Now Noyes' model atom explicitly provides this very mechanism of which we are in search, since at one part of the electronic path the two atoms cease to be drawn together and are thus able to break free from one another. It is not necessary to assume a bi-atomic molecule only; for even in a very complex structure it may be assumed that the periodic instability affects one bond frequently in comparison to the recurrence of instability in the other atomic junctions of the molecule.

A concrete example may serve to make this point clearer. The compound tetramethyl-ammonium hydroxide, when dissolved in water, yields a hydroxyl ion and the positive ion $(CH_3)_4N$.



Here, according to Noyes' conception, an electron which originally rotated under the influence of both the oxygen and nitrogen atoms has now been removed entirely from the sphere of attraction of the nitrogen and has transferred itself to the oxygen system. The neutrality of the tetramethyl-ammonium hydroxide is thus replaced by the generation of a negative charge upon the hydroxyl radicle and a corresponding positive charge on the ammonium ion. Meanwhile all the other electrons in the two systems continue to follow the normal course, each vibrating under the joint influence of the two atoms which they serve to unite. Periods of instability occur, of course, even in the case of these comparatively stable junctions, but they are assumed to be so brief or so infrequent that few ruptures occur.

When tetramethyl-ammonium hydroxide is heated, a different series of phenomena is observed. The molecule breaks down and methyl alcohol is produced. On the Noyes' hypothesis, this can be accounted for in the following way:—



Digitized by Google

In the first stage of the reaction, owing to the change in physical conditions, the electron forming the junction between the methyl group and the nitrogen passes completely into the nitrogen system, making the methyl group electrically positive. Simultaneously (if the breakdown is to occur) an electron falls from its position under the common influence of nitrogen and oxygen into the exclusive sphere of the oxygen atom. At this stage in the process, the nitrogen atom has gained an electron and lost one, leaving it in the same state as before. On the other hand, the union between nitrogen and carbon and the union between nitrogen and oxygen has been broken; and the methyl group has acquired a negative electron whilst the hydroxyl group has lost one. The two groups are thus drawn to one another and produce methyl alcohol, in which the electron moves in a stable orbit around both the carbon and the oxygen atom.

8. *Stewart's Atom.*

This model atom[1] was devised to account for chemical and radioactive phenomena; but it is not intended to supply an explanation of spectral series. The main features of it are: (1) a core of negative electrons; (2) an intermediate zone occupied normally by positive electrons but containing also, in the case of the radio-elements at least, certain negative electrons; and (3) an external region occupied by negative electrons.

The orbits of the electrons in the two inner zones are assumed to be approximately circular; the outermost electrons travel in elongated elliptical orbits.

The core is assumed to be the origin of the electrons ejected from radio-elements during β-ray changes; the intermediate zone generates α-particles; whilst the outermost electrons are those which play a part in ionic and other normal chemical reactions. The two inner regions correspond to Rutherford's positive nucleus. The atomic number of the element corresponds to the surplus of positive over negative charges in the two inner zones jointly.

The elongated elliptical orbits of the valency electrons, which may be termed "cometary electrons" for convenience, serve to account for two important chemical facts. In the first

[1] A. W. Stewart, *Phil. Mag.*, 1918, **36**, 326.

Digitized by Google

place, it is necessary to explain why changes of valency in an atom require comparatively small expenditures of energy; and in the second place, it is essential to throw some light upon the alteration in chemical and physical character of the atom produced by changes in valency. Now when the cometary electron is in aphelion to the nucleus, it is far removed from the centre of attraction and is travelling slowly in its orbit, both of which conditions will render it easily removed from or replaced in its normal path with slight expenditure of energy. Again, when at perihelion, these cometary electrons are assumed to pass very close to the outside of the positive zone; and they will affect the electrons in this zone in the same manner as the negative electrons of the core do from the inside of the ring. A change in the number of electrons in the cometary orbits will therefore influence the positive zone just as it would be affected by a change in the number of electrons in the core. The two effects, however, though alike, are not identical; for in the case of the core electrons their influence is a constant one; whereas the cometary electrons only exert a periodic influence, since during a large portion of their path they are far away from the positive zone. Thus a change in the number of the core electrons produces a permanent effect and changes the atomic number of the atom; while a change in the number of the cometary electrons tends in the same direction but is not so marked in its action. The latter influence, therefore, produces only a change in chemical character approaching to but not identical with a change in atomic number. For example, the conversion of ferric iron into ferrous iron produces a material very like magnesium, but not isotopic with it; and the conversion of hexavalent uranium into quadrivalent uranium yields a substance closely akin to thorium, but not isotopic with it.

9. *Conclusion.*

It seems desirable to sum up the subject at this point; and this can best be done by indicating very briefly the successes and failures of the various model atoms from the chemical standpoint.

Bohr's atom appears to be considerably overrated, especially by those who seem to have accepted it blindly without applying any critical examination. It appears to have failed when

Digitized by Google

attempts were made to utilise it in the case of helium and heavier elements. Thus even in the field of spectral series it is not an unblemished success. As far as chemical and radio-chemical problems are concerned, it is quite worthless. In fact it makes no pretence to offer an explanation of any of the commoner phenomena of chemistry.

Nicholson's atom is of more interest from the chemical standpoint, especially in view of his work on nebulium. With regard to atomic architecture, however, it seems doubtful if much purpose is served by attempting to build up complexes of elements and proto-elements in order to produce totals numerically equal to the atomic weight of some fresh element. The atomic weights of the elements appear, at the present day, to be among those elemental properties from which least is to be expected; and the mere juggling of figures to produce co-incidental values seems more or less a waste of time when the really important matter—the chemical properties—is left out of account entirely. For example, there appears to be very little use in pointing out that atoms of argon and of calcium may each be built up from ten helium atoms when no attempt is made to explain how the ten helium nuclei are arranged in the two cases so as to produce respectively an inert gas and a divalent metal.

G. N. Lewis' atom, as extended in scope by Langmuir, appears to be a more interesting speculation from the chemist's point of view. It is, however, only a sketch as yet; for it leaves out of account much of the information which has been acquired on the radioactivity side; and it seems doubtful if a static atom can be said to be satisfactory at the present day. The velocities with which electrons are ejected from the radio-elements appear to make it more probable—though not certain—that the internal machinery of the atom is in rapid motion; and it is difficult to conceive that a static grouping of electrons could be permanently stable. The Lewis-Langmuir atom, of course, makes no attempt to account for line spectra.

Noyes' atom is even more sketchy than the Lewis-Langmuir model, though it has attractions of its own within its limited scope. It is really devised to account purely for the attraction retaining together two or more atoms; and it would be pressing the matter too far to demand more from it.

Digitized by Google

Stewart's atom makes no pretence to account for the spectral evidence; but it seems to fit the chemical evidence as a whole better than any of the others. On the principles of pure Newtonian dynamics it is an unstable system,[1] but on the same assumption the Rutherford nucleus itself could hardly be capable of permanent existence.

From the foregoing it will be seen that up to the present no model atom has been devised which is capable of accounting for all the phenomena which a correct model atom should express. Possibly from a fusion of some of the above ideas with new material a satisfactory model may be devised in future.

[1] Jackson, *Phil. Mag.*, 1919, **38**, 256.

Digitized by Google

Digitized by Google

BIBLIOGRAPHY.

THE following notes on the literature of the subjects dealt with in this volume are not intended to be complete; they are to be regarded rather as finger-posts to guide the reader should he desire fuller information from other works. English authorities have been given wherever possible; as nowadays there are good monographs in our own language upon many subjects and we have become much less dependent upon the Germans for this kind of work. It cannot be too often impressed upon the student that his interest in chemistry will be greatly increased and his perspective of the subject improved if he will take the trouble to pursue a course of reading quite outside the range of the text-books. A comparison between a subject in a book and the same subject as handled in the original papers will very soon reveal points of interest which will probably stimulate him to further reading and certainly will enliven the subject whatever it may be.

The connection between chemical structure and the physical properties of substances has been very fully described in Smiles' *The Relations between Chemical Constitution and Some Physical Properties*, which treats the subject up to 1910. It is the only complete work dealing with this field of physical chemistry.

Information with regard to double salts is to be found in van't Hoff's *Bildung und Spaltung von Doppelsalzen*, which contains a full account of his fundamental researches in this branch. Clibbens' *Principles of the Phase Theory; Heterogeneous Equilibria between Salts and their Aqueous Solutions* deals with more recent work on the subject. Shorter accounts are given in Bancroft, *The Phase Rule*, and Findlay, *The Phase Rule*. Willard Gibbs' collected *Scientific Papers* may be consulted by those interested in the thermodynamical side of the problem.

An account of the researches of van't Hoff and his colleagues upon the Stassfurt deposits is given by him in a two-volume pamphlet, *Die Ozeanischen Salzablagerungen*.

With regard to complex salts and complex ions, the best account of the ionic problem is to be found in Jaques' *Complex Ions*.

Digitized by Google

Werner's *New Ideas on Inorganic Chemistry* contains a vast number of examples of complex salts. An account of the cobalt-ammines is given in Stewart's *Stereochemistry*.

There is no book or pamphlet dealing with the pseudo-acids, though short accounts of them are to be found in some text-books on physical chemistry. It may be well to put the reader on his guard, however, for in the case of at least one large text-book it is quite apparent that the author either never consulted the original papers or has read them quite uncritically, since criteria which Hantzsch himself abandoned at an early stage are quoted in this book as though they still held good.

The whole subject of indicators has been very fully described by Prideaux in a book devoted to this field. Both theoretical and practical questions are dealt with in the volume.

No collected account of Walden's work has yet appeared. The reader must refer to the original papers for further information.

General accounts of colloids are to be found in the following works: Burton, *The Physical Properties of Colloidal Solutions;* Freundlich, *Kapillarchemie;* Hatschek, *Colloids;* Pöschl, *Chemistry of Colloids;* Taylor, *The Chemistry of Colloids;* Zsigmondy, *Colloids and the Ultramicroscope.* Wo. Ostwald's *Handbook of Colloid Chemistry* is not complete and is very diffusely written. In connection with the same subject, it may be well to mention Michaelis's *Dynamik der Oberflächen* and Willows and Hatschek's *Surface Tension.* Butschli's *Microscopic Foams and Protoplasm* contains an account of some gel-structures. A series of reports upon technical applications of colloids appeared in the British Association Report for 1917. Bancroft's *Applied Colloid Chemistry* should be consulted.

The Brownian movement is fully described in the books, mentioned above, by Burton, Taylor, Zsigmondy and Ostwald. Svedberg's *Existenz der Molekülle* may also be consulted. An account of Perrin's researches is to be found in his work on *Atoms.*

The same volume contains a description of Perrin's work on emulsions and also a fairly complete description of many of the methods by which Avogadro's constant may be determined. The last-named subject is also dealt with, though not fully, in Millikan's *The Electron.*

Accounts of adsorption are to be found in Taylor's *Chemistry of Colloids;* Phillip's *Physical Chemistry and its Application to Medicine;* and in Hatschek's *Colloids.* The problem of surface action is dealt with in Michaelis's *Dynamik der Oberflächen.* A shorter account is to be found in Willows and Hatschek's *Surface Tension.*

Digitized by Google

Some theories of colloidal solution are dealt with in Burton's *Physical Properties of Colloidal Solutions*, and others are given in Pöschl's *Chemistry of Colloids*.

Further information on catalysis may be sought in Henderson's *Catalysis;* Jobling's *Catalysis and its Industrial Applications;* and in Rideal and Taylor's *Catalysis in Theory and Practice*.

A full account of emission spectra is given in Baly's *Spectroscopy* and in Sommerfeld's *Atombau und Spektrallinien*. A shorter account of this part of the subject is to be found in Konen's *Leuchten der Gase und Dämpfe*. For an account of phosphorescence spectra, Urbain's *Spectroscopie* may be consulted. The fullest work on the whole subject is Kayser's *Handbuch der Spektroskopie*.

Friend's *Theory of Valency* gives accounts of the various hypotheses which have been suggested with regard to chemical affinity. The electronic views of valency are discussed in Fry's *Electronic Conception of Valence*.

On the subject of the Periodic Law, works have been written by each of the three authors who were mainly responsible for its discovery. Newlands reprinted his original papers in a small volume, *The Discovery of the Periodic Law;* Mendeléef's views are to be found in his *Inorganic Chemistry*, the footnotes of which are often very much more interesting than the text they amplify; whilst Lothar Meyer's *Modern Theories of Chemistry*, though published in 1888, still retains a certain freshness. The fullest account of the progress of investigation in this branch of chemistry is to be found in Venables' *Development of the Periodic Law*, which contains summaries of more than 250 papers on the subject. Rudorf's *Periodic Classification and the Problem of Chemical Evolution* is a smaller volume. Garrett's *Periodic Law* contains a very good account of the main periodic properties of the elements. Chapters on the Periodic Law are to be found in Pattison Muir's *Development of Chemical Theories and Laws;* Soddy's *Matter and Energy;* Letts' *Fundamental Problems of Chemistry Old and New;* and Stewart's *Recent Advances in Physical and Inorganic Chemistry*. The relationship between radioactivity and the Periodic Law is dealt with in Soddy's *Chemistry of the Radio-elements*, Part II.

No full account of atomic structure from the chemical standpoint has yet been given in book form. Some of the physical views on the subject are given in Thomson's *Corpuscular Theory of Matter;* Richardson's *Electronic Theory of Matter;* and Sommerfeld's *Atombau und Linienspektren*. The Lewis-Langmuir and

Digitized by Google

Bohr atoms are described in Loring's *Atomic Structure*. The best short account of Bohr's model atom is to be found in Millikan's *The Electron*. Three lectures on the problem of the elements, by Soddy, Nicholson and Jeans, are printed in the *Transactions of the Chemical Society* (1919).

It must be borne in mind by the student, however, that although books are convenient for reference purposes and for acquiring a general knowledge of any subject about which one knows very little, nevertheless the perusal of a book does not bring one into direct touch with research, and the real source of interest is to be found in the original papers. The continual reading of books, to the neglect of first-hand acquaintance with chemical journals, is apt to produce a totally false impression of the difficulties of research work and also to leave the feeling of a "cut-and-dried" subject, owing to the unavoidable process of summarisation which the material has to undergo if it is to be brought within reasonable compass. In that summarisation, much that is tentative in an original paper cannot but be handled in a more dogmatic fashion in the book; and in this way false perspectives are almost unavoidable.

It is best, then, to regard books mainly as guides to the original literature; and to consult the latter whenever any interesting subject is unearthed in book form. As a guide to recent literature, the *Annual Reports of the Chemical Society* will probably serve to assist the student; but it must be remembered that the subjects described in them from year to year represent only a fraction of the work actually done.

Digitized by Google

APPENDIX.

TABLE I.

List of Elements Examined with the Mass-spectrometer.[1]

Where isotopes have been detected, their masses are given in the order of the intensity of the lines which they produce in the mass-spectroscope. The intensity is probably a measure of the percentage of the corresponding isotope in an ordinary specimen of the element. Bracketed figures are provisional only.

Element.	Atomic Number.	"Atomic Weight."	Masses of Atoms Detected.
Hydrogen . .	1	1·008	1·008
Helium . . .	2	3·99	4
Lithium . . .	3	6·94	7, 6
Boron . . .	5	10·9	11, 10
Carbon . . .	6	12·00	12
Nitrogen . .	7	14·01	14
Oxygen . . .	8	16·00	16
Fluorine . .	9	19·00	19
Neon . . .	10	20·2	20, 22 (21)
Sodium . . .	11	23·00	23
Silicon . . .	14	28·3	28, 29 (30)
Phosphorus . .	15	31·04	31
Sulphur . . .	16	32·06	32
Chlorine . . .	17	35·46	35, 37 (39)
Argon . . .	18	39·88	40 (36)
Potassium . .	19	39·1	39, 41
Arsenic . . .	33	74·96	75
Selenium . .	34	79·2	No isotopes clearly shown
Bromine . . .	35	79·92	79, 81
Krypton . . .	36	82·92	84, 86, 82, 83, 80, 78
Rubidium . .	37	84·77	85, 87
Tin	50	118·7	No isotopes clearly shown
Antimony . .	51	120·2	,, ,, ,, ,,
Tellurium . .	52	127·5	,, ,, ,, ,,
Iodine . . .	53	126·92	127
Xenon . . .	54	130·2	129, 132, 131, 134, 136 (128, 130?)
Caesium . . .	55	132·81	133
Mercury . . .	80	200·6	(197-200), 202, 204

[1] Aston, *Trans.*, 1921, **119**, 676; *Phil. Mag.*, 1921, **42**, 140, 436.

Digitized by Google

TABLE II.

List of Isotopes Discovered by Radioactivity Methods.

The atomic weights attributed to the elements below have been deduced from the loss of α-particles from uranium and thorium.[1] To simplify the printing, only the round numbers have been given. If the atomic weight of uranium be taken as 238·2 and that of thorium as 232·2, all the values below must be increased by 0·2 units.

Group.	Atomic Number.	Isotopes.
0	86	Niton = 222; Actinium emanation = 218; Thorium emanation = 220.
IIa	88	Radium = 226; Actinium-X = 222; Mesothorium-1 = 228; Thorium-X = 224.
IIIa	89	Actinium = 226; Mesothorium-2 = 228.
IIIb	81	Radium-C_2 = 210; Actinium-D = 206; Thorium-D = 208; Thallium = 204.
IVa	90	Uranium-Y? Uranium-X_1 = 234; Ionium = 230; Radioactinium = 226; Thorium = 232; Radiothorium = 228.
IVb	82	Radium-B = 214; End-product of Ra-C_2 = 210; Radium-D = 210; Actinium-B = 210; Actinium end-product = 206; End-product of Th-D = 208; End-product of Ra-F = 206; End-product of Th-C′ = 208; Common lead (mixture) = 207.
Va	91	Uranium-X_2 = 234; Eka-tantalum = 230.
Vb	83	Bismuth = 208; Radium-C = 214; Radium-E = 210; Actinium-C = 210; Thorium-C = 212.
VIa	92	Uranium-1 = 238; Uranium-2 = 234.
VIb	84	Radium-A = 218; Radium-C_1 = 214; Radium-F* = 210; Actinium-A = 214; Thorium-A = 216; Thorium-C′ = 212.

No isotopes have been discovered by radioactivity methods in the following Groups: Ia, Ib, IIb, VIIa, VIIb and VIII.

TABLE III.

List of Isobares among the Elements Heavier than Mercury.

(See note on atomic weights in Table II.)

Atomic Weight.	Isobares.
234	Uranium-X_1; Uranium-X_2; Uranium-2.
230	Ionium; Uranium-Y; Eka-tantalum.
228	Mesothorium-1; Mesothorium-2; Radiothorium.
226	Radium; Actinium; Radioactinium.
222	Niton; Actinium-X.
218	Radium-A; Actinium emanation.
214	Radium-B; Radium-C; Radium-C_1; Actinium-A.
212	Thorium-B; Thorium-C; Thorium-C′.
210	Radium-C_2; Radium-D; End-product of Ra-C_2; Radium-E; Radium-F; Actinium-B; Actinium-C.
208	Thorium-D; End-product of Th-D; End-product of Th-C′.
206	Actinium-C; End-product of Actinium; End-product of Ra-F.

[1] See Soddy's chart, *Trans.*, 1919, **115**, 16.

* Polonium.

Digitized by Google

NAME INDEX.

Abegg, 303-6, 363.
Aberson, 295.
Acree, 269.
Adams, 327.
Adriani, 58.
Alexandroff, 164.
Appleyard, 244-5.
Archibald, 49, 55, 129.
Armitage, 291.
Arrhenius, 269, 271, 291, 308.
Aston, 155, 336, 337, 388, 403.
Auld, 261.
Auwers, 13, 291, 292.
Avogadro, 209-30.

Bache, 188.
Baker, 264.
Balcom, 261.
Balmer, 283.
Baly, 35.
Bancroft, 258, 265, 399, 400.
Bauer, 12, 19.
Baur, 129.
Bayliss, 248.
Beans, 291.
Bechold, 161.
Bedson, 320.
Benson, 236.
Berneck, 174.
Berthelot, 214, 256.
Berthollet, 290.
Berzelius, 290, 319.
Bigelow, 258.
Billitzer, 252-3.
Biltz, 180.
Bingham, 129.
Blair, 50.
Blaise, 107.
Blake, 167.
Bodländer, 303.
Bohr, 339, 382-5, 395.
Boisbaudran, 285-6.
Boltwood, 225.
Boyd, 261.
Bragg, 226, 227, 228.
Bredig, 116, 162, 174, 252, 257, 258, 260, 261, 264.
Bremer, 46.
Briggs, 231, 302, 309.
Brillouin, 216.
Broglie, 193
Brown, 186, 257.
Bruhl, 18, 19.
Buchner, 129.
Burton, 169, 191, 400, 401.
Bütschli, 250, 400.

Cady, 134.
Cannizzaro, 319
Carnelley, 316, 328.
Carrara, 129, 134.
Carrol, 129, 157.
Cassius, 162.
Caven, 350.
Centnerszwer, 129, 154.
Chancourtois, 315-6.
Chappuis, 231.
Chaudesaigues, 188, 192.
Clarke, 15.
Claus, 296.
Clausius, 213.
Clibbens, 399.
Cone. 307.
Cooke, 313.
Couper, 196.
Crookes, 275, 278, 316, 329-32, 338, 365.
Crymble, 33, 36, 37, 391.

Dabrowski, 188.
Dalton, 311.
Dancer, 186.
Davidson, 100.
Davis, 232.
Davy, 128.
De, 309.
Devaux, 211.
Dewar, 238, 357.
Ditte, 286.
Dixon, 264.
Doebereiner, 312.
Donnan, 251-2.
Drude, 149.
Dumas, 313, 314, 319, 344.
Dunstan, 49.
Dutoit, 129, 155.

Ehrenhaft, 193.
Ehrlich, 261.

Digitized by Google

Einstein, 191, 192, 216, 217.
Eisenlohr, 18.
Elissafof, 172.
Erlenmeyer, 12, 291.
Ernst, 255, 258.
Euler, 105, 108, 110.
Eykman, 18.

Fajans, 260.
Falk, 291.
Faraday, 128, 162, 165, 181, 265.
Feist, 261.
Findlay, 51, 57, 19.
Fischer, E., 261-2.
Fiske, 260.
Fleck, 377.
Flurscheim, 12.
Foster, 319.
Fränkel, 264.
Frankland, 196.
Franklin, 129-34.
Freund, 291.
Freundlich, 178, 179, 234, 240, 241, 400.
Friend, 291, 302-3, 369, 401.
Frowein, 46.
Fry, 291, 307, 401.
Fulhame, 264.

Garrett, 401.
Gay-Lussac, 312.
Geiger, 224, 225.
Gibbs, 234, 399.
Gladstone, 313.
Glendinning, 33.
Gmelin, 313, 319.
Gomberg, 307.
Gore, 130,
Gorke, 105.
Gouy, 187, 188.
Graham, 159-61, 163, 247.
Green, 118.

Häckel, 12.
Hall, 316, 344, 365.
Haller, 25.
Hantzsch, 98, 100, 101, 102, 103, 104, 105, 106, 107, 108, 109, 110, 115, 117, 118, 119, 400.
Hardy, 170, 177, 252.
Harkins, 316, 344, 365, 389.
Harper, 112.
Harries, 12.
Hartley, E., 300.
Hatschek, 400.
Hautefeuille, 286.
Heen, 291.
Henderson, 401.
Henri, 33, 189.
Henry, 231, 232, 238.
Hevesy, 342.
Hewitt, 29, 30.
Hilditch, 25, 26, 291.
Hinrichsen, 12, 43.
Hittorf, 89.
Hofmeister, 183, 250.
Holleman, 98, 99.

Ikeda, 174.

Jackson, 397.
Jacobson, 293.
Jaques, 84, 399.
Jeans, 214, 402.
Jevons, 186.
Jobling, 401.
Johonnot, 210.
Jones, 49, 55, 129, 154, 301.
Jörgensen, 297.

Kablukoff, 153.
Kahlenberg, 129.
Kauffmann, 105, 106, 291.
Kayser, 283-4, 401.
Keeson, 215,
Kekulé, 196, 292.
Kenyon, 25.
King, 118.
Kipping, 261.
Knoevenagel, 291.
Knorr, 291.
Knox, 85.
Konen, 401.
Krapiwin, 156.
Kraus, 129, 131, 132.
Kremann, 116.

Lampa, 166.
Lander, 350.
Langevin, 191.
Langmuir, 266, 390-1, 396.
Lapworth, 269.
Le Bel, 197, 291, 295.
Le Blanc, 85, 87.
Le Chatelier, 44, 145.
Lehmann, 248.
Leighton, 12.
Letts, 401.
Leverrier, 327.
Levier, 129.
Lewis, G. N., 390-1, 396.
— W., 243, 272.
Linder, 161, 168, 169, 177, 180, 181.
Lindsay, 55, 129, 156.
Lockyer, 365.
Lorenz, 215.
Loring, 402.
Lossen, 296.
Lottermoser, 180, 181, 185.

Macbeth, 15, 33, 34, 112.
McBain, 232.

Digitized by Google

McClelland, 309.
McIntosh, 129.
McKeown, 50.
McMaster, 129, 157.
Magini, 32.
Marcelin, 271.
Marignac, 312.
Martin, 368.
Marx, 122.
Matthews, 129.
Mauguin, 248.
Maxwell, 212, 374.
Mayer, 369.
Meade, 188.
Mellor, 255, 265.
Mendeléef, 316, 320-4, 326-8, 331-4, 346, 348, 353, 355, 356, 361-3, 368, 401.
Meyer, E., 291.
— L., 320, 324-6, 359-61, 401.
— K., 118.
— R., 28, 122.
— V., 97, 291, 293-4.
Michael, 12, 98.
Michaelis, 400.
Milliken, 194, 223, 224, 229, 383-4, 400, 402.
Milner, 236.
Moeller, 185.
Moissan, 358.
Moseley, 275, 340, 353.
Mossotti, 213.
Mouton, 169.
Muir, 291, 401.
Müller, 50.
Muller, 19, 111.
Mumme, 291.
Murray, 156.

Nelson, 291.
Nernst, 136, 149, 358.
Newlands, 315-22, 401.
Nicholson, 386-8, 396, 402.
Nirdlinger, 269.
Noyes, 85, 87, 144, 391-3, 396.

Onnes, 215.
Ostwald, W., 113, 114, 116, 118, 119, 127, 184, 195-7, 269.
— Wo., 166, 233, 400.

Paneth, 342.
Partington, 126.
Pascal, 20, 21.
Pauli, 170.
Pearson, 374.
Perkin, A. G., 118.
— Sir W. H., 19, 21
Perrin, 4, 161, 170, 172, 173, 188, 198-208, 211, 216-9, 226, 228, 229, 248, 249, 270, 271, 400.
Petersen, 297.
Pettenkofer, 313.
Phillip, 400.
Pickard, 25.
Picton, 161, 168, 169, 177, 180, 181.
Planck, 220, 221, 222.
Pöschl, 400.
Precht, 286.
Preston, 285.
Prideaux, 400.
Prout, 312, 373.

Quincke, 171.

Ramage, 286.
Ramsay, 190, 291, 309, 333.
Rankine, 214.
Raoult, 198.
Rayleigh, 211, 215, 216, 316, 333.
Rea, 33.
Regener, 225.
Reinders, 174.
Reinold, 210.
Retgers, 43.
Reynolds, E., 370-2.
— O., 375.
Richardson, 401.
Rideal, 265, 401.
Riecke, 291, 294.
Roloff, 88.
Roozeboom, 40.
Rosenthaler, 261.
Roth, 13.
Rucker, 210.
Rudorf, 401.
Ruhoff, 129.
Runge, 283-4, 286.
Rupe, 25.
Rutherford, 224, 225, 339, 378, 379, 381, 397.
Rydberg, 283-4, 286, 340, 344.

Sabaneieff, 164.
Sabatier, 268.
Sachse, 291.
Sachsel, 43.
Sammet, 144.
Saussure, 237.
Scacchi, 43.
Schlamp, 138.
Schlundt, 129.
Schmidt, 358, 365, 368.
Schönrock, 55.
Schroeder, 183.
Schultze, 98.
Schulze, 177.
Seddig, 192, 193.
Senderens, 268.
Senter, 269.
Sherill, 85, 86.
Smedley, 19.

Digitized by Google

Smiles, 23, 273, 399.
Smoluchowsky, 191, 215.
Snethlage, 269.
Soddy, 316, 335, 336, 338, 339, 340, 344, 353, 354, 359, 365, 377, 401, 404.
Sodeau, 255.
Sommerfeld, 401.
Spiegel, 291, 303.
Spiro, 250.
Steele, 129.
Stewart, 13, 15, 32, 33, 34, 35, 36, 307, 316, 337, 338, 355, 369, 394, 397, 400, 401.
Stieglitz, 116.
Stokes, 200, 217, 223.
Stoney, 316.
Sutherland, 214.
Svedberg, 162, 177, 187-9, 400.
Swan, 277.

Tanatar, 256.
Taylor, 168, 169, 184, 236, 242, 400, 401.
Tesla, 27.
Thiele, 9, 11, 12, 13.
Thole, 49.
Thomsen, 333.
Thomson, Sir J. J., 136, 154, 234, 266, 291, 306-7, 336, 401.
Tinkler, 88.
Titoff, 231, 255.
Townsend, 223.
Traube, 149.
Trooste, 286.
Turbaba, 257.
Twitchell, 266.
Tyndall, 165.

Urbain, 401.
Usiglio, 61, 62.

Van Bemmelen, 182, 250.
— den Broek, 339.
— der Waals, 197, 214.
Van't Hoff, 14, 43, 44, 45, 46, 48, 49, 50, 62-82, 197, 235, 291, 292, 343, 399.
Vaubel, 291.
Veazey, 129.
Venables, 401.
Voegelen, 109.
Vorländer, 12, 248, 291.

Walden, 4, 129, 134-54, 307, 400.
Walker, Sir J., 244-5.
Watts, 286.
Webster, 384.
Wedekind, 261, 301.
Weimarn, 247-9.
Werner, 93, 94, 291, 295-304, 400.
Whitney, 167.
Widal, 179.
Wiedemann, 170.
Williams, 231.
Willows, 400.
Wilson, C. T. R., 223, 253.
— E., 389.
— H. A., 223.
Wislicenus, 291.
Wolf, 386, 387.
Wright, 33, 34, 36.
Wunderlich, 291.
Wurtz, 286.

Zangger, 217.
Zawidski, 236.
Zelinsky, 156.
Zeeman, 284-5.
Zsigmondy, 162, 165, 166, 181, 187, 400.

Digitized by Google

SUBJECT INDEX.

α-PARTICLES, 224, 225, 226.
α-rays, 378, 379.
Abnormal hydrates, 102, 109.
— hydrolysis, 102, 104.
— temperature coefficients, 102, 107.
Absorption, 232.
— general, 31.
— selective, 32.
— spectra, 31.
— — and conjugation, 33 ff.
— — — valency, 37.
— — of ions, 37.
Acetaldehyde, 133, 257.
Acetanilide, 31.
Acetic acid, 110, 137, 138, 156, 240, 241, 242, 244, 259, 263.
Acetone, 13, 35, 137, 141, 152, 157.
Acetonitrile, 137, 139, 141, 146, 148, 152.
Acetonylacetone, 35.
Acetyl chloride, 137, 141.
Acids, fatty, 26, 27.
Aci-form, 98.
Actinium-X, 335.
Active molecules, 271.
Adhesion, 251.
Adipic acid, 27.
Adsorption, 182, 231 ff.
— and catalysis, 265.
— — chemical reaction, 243.
— in gas-liquid systems, 239.
— — gas-solid systems, 237.
— — liquid-solid systems, 239.
— — two immiscible liquids, 242.
— isothermal, 240.
— negative, 235.
— positive, 235.
— selective, 265-6.
Affinity, 289 ff.
— residual, see Residual Affinity.
Agar, 168.
Agglutination, 179.
Air lines, 280.
Albumins, 159, 167, 168, 170, 173, 181, 182.
Alcogels, 160.
Alcohol, 134, 242, 250, 251, 263.
Alcoholates, 305.
Alcohols, as ionising solvents, 134.
Alcosols, 160.
Alkali metals, 323, 325, 344, 347, 363.
— — and thallium, 349.
Alkyl derivatives of elements, 363.
Aluminium, 287, 325, 345, 354.
— acetate, 162-3.
— and beryllium, 351.
— — chromium, 351.
— hydroxide, 132, 159, 168, 243.
— nitrate, 179.
— oxide, 172.
— — gel, 182.
— sulphate, 40, 177.
— trimethyl, 163.
Alums, 40, 349, 351.
Amino-acetic acid, 96.
Ammonia, 237, 256.
— liquid, properties of, 129.
— — reactions in, 129 ff.
— reaction of pseudo-acids, 109.
Ammoniates, 305.
Ammonium compounds, 131, 184, 305.
Ammono-acids, 130.
Ammono-bases, 130.
Ammonolysis, 134.
Ammono-salts, 130.
Amphoteric electrolytes, 96.
— elements, 345-6.
Amyl alcohol, 153.
Anhydrite, 60, 62.
Aniline, 30, 31, 257.
Anomalies in Periodic System, 334, 338.
Anomaly, optical, 17.
Antimony, 363.
— chlorides, 153.
— sulphide sol, 168.
Antipodes, optical, 43, 51, 56 ff.
Arc spectra, see Spectra.
Argon, 214, 238, 333, 336, 344, 354, 365.
Arsenic, 363.
— trichloride, 154.
Arsenious sulphide sol, 161, 168, 169, 175, 178, 179.
Ascherite, 77.
Astrakanite, 44, 51 ff., 74-8, 80-2.
"Astronomical" elements, 365.
Asymmetry, 260-1.

Digitized by Google

Atmosphere, artificial, 208.
Atom, model, 382 ff.
— Saturnian model, 381.
— vortex, 374.
Atomic architecture, 388-9.
— masses, values of, 229.
— nucleus, 361, 378 ff., 394-5.
— numbers, 276, 338, 355, 394, 403, 404.
— — and atomic volumes, 342.
— — — — weights, 341, 343, 379.
— — — elemental properties, 341.
— — — spectra, 275-6, 287-8, 340.
— — — X-ray spectra, 340.
— — of rare earth elements, 358.
— order, 338, 360.
— structure, 373 ff.
— volume curve, 325 ff.
— volumes, 347, 358 ff., 363, 369.
— — elements of equal, 343.
— — of isotopes, 337.
— — and atomic numbers, 342.
— — — electronics, 359.
— weight and atomic number, 341, 343, 379.
— weights an integral number, 312, 337.
— — corrected by Periodic Table, 326.
— — and chemical properties, 330.
— — — Periodic Law, 312 ff., 334 ff.
— — — spectra, 285, 286.
Auto-catalysis, 258.
Auto-retardation, 258, 259.
Auxochrome, 90.
Avogadro's constant, 209 ff.
— — accurate value of, 229.
— — definition of, 209.
— — table, 229.
— — and emulsions, 216.
— — — gaseous ions, 222.
— — — kinetic theory, 211.
— — — radiation, 219.
— — — radioactivity, 224.
Azelaic acid, 27.
Azoxy-anisol, 248.

β-RAY changes, 377, 394.
β-rays, 377, 378, 380.
Bacteria, agglutination of, 179.
Band spectra, 274.
Barium, 287, 288, 362.
— salts, 172, 178, 179.
Benzaldehyde, 258, 260.
Benzene, 30, 240, 242, 266.
— formula, 12.
— refraction, 19.
Benzoic acid, 240, 241, 242.
Benzonitrile, 152.
Benzophenone, 308.
Benzyl alcohol, 258.
Beryllium, 351, 362, 372.
— and aluminium, 351.
— oxide, 348.
Bischofite, 74, 75.
Bismarck brown, 168.
Bismuth, 279, 314, 342, 363.
— oxychloride, 134.
— sol, 168.
Black body, 220.
Boiling-point, 15.
Bonds, see Double and Triple.
Boric acid, 172.
Boron, 336.
— and carbon, 351.
— — silicon, 351.
— hydride, 351.
Brassidic acid, 34.
Brittleness, periodicity in, 325.
Bromine, 88, 153-4, 214, 242, 354.
Bromobenzene, 30, 152.
Brownian movement, 186 ff.
— — factors influencing, 191.
— — in gases, 193.
— — measurement of, 188, 191-3.
— — nature of, 186.
— — of rotation, 217.
— — and Avogadro's constant, 216.
— — — electrolytes, 188.
— — — kinetic theory, 190.
— — — viscosity, 187, 191.
Bunsen flame spectrum, 277.

CADMIUM, 359, 362.
— iodide, 89.
— sulphide sol, 168.
Caesium, 273, 285, 297, 288, 344, 345.
— chloride, 43.
Calcium, 287, 288, 343, 347, 362, 372.
— carbonate, 172.
— chloride, 131.
— magnesium potassium sulphate, see Polyhalite.
— nitrate, 131.
— sulphate, see Anhydrite.
Camera lucida, 188.
Camphor, 26.
— oximes, 57.
— quinone, 26.
Cane-sugar, 265, 268, 269.
Caramel, 164.
Carbamide (urea), 130.
Carbon, 325, 345, 363, 372.
— and boron, 351.
— dioxide, adsorption of, 231, 240, 241.
— disulphide, 258.
— monoxide, 237.
Carbonates, basic, 347-8.
— of Group I. metals, 347.
Carbonyl group reactivity, 13.
Carborundum, 172.
Carnallite, 60, 65-75, 78, 81.

Digitized by Google

Carriers, 267.
Carvenene, 13.
Catalysis, 254 ff.
— criteria of, 254.
— homogeneous and heterogeneous, 264.
— ionic, 268 ff.
— positive and negative, 257.
— selective, 261.
— theories of, 264 ff.
— and complex ions, 85.
Catalysts, poisoning of, 265.
— protective action of, 258.
Catalytic action of sols, 174-5.
— effects, secondary, 258.
Cataphoresis, 168 ff., 179.
Cell, isothermal, 220.
Cellulose, 172.
Celtium, 353.
Centrifuge, 199.
Cerium, 352.
— oxide, 356.
Charcoal, 231, 237, 238, 239, 240, 241, 242, 244.
Chemical affinity, 289 ff.
— homogeneity, 331, 335, 338.
Chloracetic acid, 242.
Chlorides, coloured, 363.
Chlorine, 154, 214, 212, 254, 329-31, 336, 343, 344.
— atomic volume of, 359, 360.
Chromium, 343, 354, 363.
— characteristics of, 351.
— compounds, 168, 172, 173, 351.
Chromophores, 115.
Cinematograph, 189.
Citraconic acid, 34.
Coagulating power and valency, 179.
Coagulation, 160, 174 ff., 182.
— concentration, 177.
— hypotheses on, 176 ff.
Cobaltammines, 91 ff., 298 ff.
— optically active, 94.
Cobalt chloride, 157, 299.
— roseo-salts, mare's nest in, 301.
Cohesion, 251, 344.
Colemanite, 77.
Colloidal solution, 158.
Colloids, 158 ff.
— charges on, 168, 179 ff.
— diffusion of, 164.
— electrical properties of, 167 ff.
— hypotheses on, 246 ff.
— irreversible, 161.
— molecular weights of, 164.
— mutual precipitation of, 18.
— optical properties of, 164 ff.
— osmotic pressure of, 164.
— preparation of, 161 ff.
— protective action of, 164.
— reversible, 161.
Colloids, size of particles in, 159, 166.
Colour change in pseudo-acids, 102, 105.
Coloured chlorides, 363.
Colours of salts, periodicity in, 325.
Columbium, 359.
— oxide, 356.
Complex ions, 83 ff.
— — and conductivity, 89.
— — in cells, 90.
— — spectra of, 88.
— — tests for, 84 ff.
— salts, 41, 83 ff., 298 ff., 305, 309, 348.
— — and Periodic System, 91.
Compressibility of gases, 212, 215.
Concentration and surface energy, 234.
— in froths, 236.
Condensation, ideal coefficient of, 212.
Conductivity in inorganic liquids, 153 ff.
— — mixed solvents, 155.
— — non-aqueous solvents, 135 ff.
— and double salts, 55.
— — solvent constitution, 134 ff.
— — — power, 142 ff.
— — transition point, 49.
— — viscosity, 141 ff.
— of complex ions, 89:
— — pseudo-acids, 100, 102, 103.
Conglomerate, 39, 59.
Congo red, 243.
Conjugated double bonds, 11 ff., 16, 18, 19, 24.
Conjugation, 8, 14.
— spatial, 14.
— and absorption spectra, 33 ff.
— — addition reactions, 9 ff. 13.
— — boiling-point, 16.
— — heat of combustion, 13.
— — magnetic rotation, 24.
— — — susceptibility, 21.
— — optical rotation, 25.
— — reactivity, 13, 15.
— — refractivity, 18.
Constant solution, 68.
Continuous spectra, 274.
Co-ordination hypothesis, 299.
Copper, 267, 285, 323.
— compounds, 55, 121, 168, 255, 257, 267, 347, 348.
— elemental characteristics of, 348.
— sol, 168.
— and mercury, 348.
— — nickel, 350.
— — thallium, 348.
Coronium, 344, 388.
Critical constants, 214.
— grain, 251.
— opalescence, 215.
Crystallisation, end-point of, 65.

Digitized by Google

Crystalloids, 159, 246, 247.
Crystals, atomic distances in, 226.
— liquid, 248.
Cuprous hydroxide, 348.
— potassium chloride, 44.
— sulphide, 348.
Cyanogen, 154.
Cyanuric ester, 33.

Deliquescence, 42.
Density and transition point, 50.
— of emulsion particles, 199.
Diacetyl, 35.
Diallyl, 18.
Dialysis, 159, 163.
Diamagnetism, 20.
Diamyl sulphide, 25.
— sulphone, 25.
— sulphoxide, 25.
Diaphragms, charged, 172.
Dielectric constants, 213.
— — lists of, 137, 146, 152.
— constant and dissociating power, 136 ff.
— — — solvent power, 150.
Dielectrics, theory of, 213.
Diffusion and Avogadro's constant, 218.
— of colloids, 164.
Dilatometer, 45.
Diluent, 280.
Dimensions, molecular, 209 ff.
Dimethyl-aniline, 30.
Dimethyl-phenylene-diamine, 30.
Dinitromethane, 108.
Diphenylamine, 244, 245.
Diphenyl-hexatriene, 19.
Diphenyliodonium hydroxide, 345.
Diphenylpyrone, 28, 29.
Dipoles, 294.
Directive influence of solvent, 263.
Dispersion, mechanical, 161.
Dissociation and refractivity, 145.
— — solubility, 143.
— in ionising solvents, 135 ff.
— table of degree in various solvents, 137.
Double bonds, 10-14, 15, 16, 18, 19, 21, 24.
— — conjugated, 11 ff., 16, 18, 19, 24.
— salts, 39 ff., 78.
— salts' existence-limits, 78.
Dust-counter, 223, 253.
Dvi-tellurium, 328.
Dyeing, 245.

e, 223, 224, 384.
e/m, value of, 385.
Efflorescence, 42.
Egg-white, 164, 176.
Eka-silicon, 327.
Electrical charges on colloids, 168, 179 ff.
— hypotheses of colloids, 252.
— methods of colloid preparation, 162.
Electric charges on diaphragms, 172.
— — and surface phenomena, 233.
Electricity and matter, 376 ff.
Electroaffinity, 363.
Electrochemical character, periodicity in, 325.
Electro-endosmosis, 170, 179.
Electrolytes and Brownian movement, 188.
— — colloids, 168.
— as coagulating agents, 175 ff.
— types of, 96.
Electrometer, capillary, 233.
Electromotive force and atomic numbers, 342.
— — — transition point, 49.
Electronic orbits, 382.
Electrons, cometary, 394.
— valency, 394.
Electrostriction, 148.
Elementary groups, 332, 335.
Elements, "astronomical," 365.
— colorogenic, 363.
— discovered spectroscopically, 273.
— homogeneous, or inhomogeneous, 329, 335.
— melting-points of, 344-5.
— orthoperiodic, etc., 371.
— still unisolated, 338.
— transitional, 332 ff.
— unisolated, 334.
— yielding alkyl derivatives, 363.
— — hydrides, 363.
— x and y, 334.
Emission spectra, see Spectra.
Emulsin, 261.
Emulsions, calculation of N from, 216.
— density of grains in, 199.
— diffusion in, 218.
— distribution of particles in, 195 ff.
— methods of observing, 204.
— preparation of, 198 ff.
— volume of grains in, 200.
Emulsoids, 160, 163, 246.
End-point of crystallisation, 65.
Energy, surface, 233.
Enhanced lines, 282.
Enzymes, lock-and-key simile, 262.
— and sols, 174.
Eosin, 168.
Equilibrium in reactions, 256.
Equimolecular mixtures of antipodes, 56.
Erbium, 353.
Erucic acid, 34.
Ethane 138, 351.
Ether, 153, 242.

Digitized by Google

Ether squirts, 375.
Ethyl alcohol, 138, 139, 156.
— cyanide, 138.
— iodide, 36.
— tartrate, 25.
Ethylene, 215.
Europium, 353.
— chlorides, 356.

Fats, 266.
Fatty acids, adsorption of, 266.
Ferments, 174.
Ferric caesium chlorides, 43.
— chloride, 43, 48, 55.
— hydroxide, 168, 177, 182.
— potassium chloride, 43, 48.
Ferrous sulphate, 42, 43.
Flame spectra, 276 ff.
Fluorescein, 29.
Fluorescence, 27, 164.
Fluorine, 305, 332-4, 358.
Fluorophore, 28.
Formaldehyde, 181, 267.
Formic acid, 156, 242.
Freezing-point method and double salts, 55.
Froths, 236.
Fructose, 261-2.
Fuchsin, 168.
Fumaric acid, 32.

Gadolinium, 353.
Galactose, 261-2.
Gallium, 273, 285, 287, 327.
Gamboge, 162.
— emulsions, 198, 199, 200, 207, 218, 219.
Gaseous ions, charges on, 222.
Gases, Brownian movement in, 193.
— compressibility of, 212, 215.
— viscosity of, 212, 214.
Gas molecules, distribution in vertical column, 201.
Gelatine, 159, 163, 170, 172, 176, 181-5, 250.
Gels, 160.
— absorptive power of, 183.
— conversion to sols, 163.
— elastic, 182, 183.
— lyophilic, 182.
— lyophobic, 182.
— properties of, 182 ff.
Germanium, 327, 363.
Gläserite, 74, 75, 81.
Glauberite, 77.
Glauber's salt, 78, 79, 80.
Globulin, 169.
Glucose, 261-2.
Glucosides, 262.
Glutaconic ester, 107.
Glutaric acid, 27.
Glycerine, 219.
Glycerogels, 160.
Glycerosols, 160.
Glycol, 148, 150.
Gold, 285, 323, 342, 350, 378.
— atom, 381.
— chlorides, 162, 181, 347, 349, 350.
— hydroxide, 349.
— number, 181.
— sols, 162, 166, 168, 181, 187, 249.
— sulphide, 349.
— translucent, 210.
— and thallium, 349.
Gum-arabic, 163, 181.
Gum tragacanth, 182.
Gypsum, 77.

h, 222.
Hæmoglobin, 168.
Halogens, 325, 344, 345, 357-8, 363. See also Separate Elements.
Heat of combustion, 13.
Helium, 225, 238, 333, 343, 344, 346, 358.
— atom, 388.
— spectrum, 385.
Helix, telluric, 315.
Heptylic acid, 236.
Heterobaric heterotopes, 338.
— isotopes, 338.
Hexadiene, 18.
Holmium, 353.
Homogeneity, chemical, see Chemical homogeneity.
Hydrates, 41, 44, 49, 50, 305.
— abnormal, 109.
Hydrazine, 307.
Hydride-forming elements, 363.
Hydrides, metallic, 357.
— in catalysis, 268.
Hydriodic acid, 153.
Hydro-acids, 130.
Hydro-bases, 130.
Hydrobromic acid, 153.
Hydrochloric acid, 153, 260, 267, 270.
Hydrocyanic acid, 154, 174, 258, 260.
Hydrogels, 160.
Hydrogen, 237, 238, 239, 254, 255, 271, 325, 337, 344, 388.
— and alkali metals, 357.
— — halogens, 357.
— atom, weight of, 230.
— chloride, 237, 257.
— ions as catalysts, 268 ff.
— peroxide, 154, 257.
— position in Periodic Table, 357.
— spectrum of, 381-2, 385.
— sulphide, 153, 237, 283.
Hydrolysis method of preparing colloids, 162.

Digitized by Google

Hydro-salts, 130.
Hydrosols, 160.
Hydroxylamine, 256.

Immunity of sols, 178.
Indication, mechanism of, 123.
Indicators, rule for use of, 125.
— and transition point of hydrates, 50.
— intramolecular change, theory of, 115.
— ionic hypothesis of, 113.
Indigo, 168.
Indium, 273, 287, 354.
Inert elements, see Zero group and individual names.
"Inseparable" elements, 336.
Instability, molecular, 392.
Internal friction, see Viscosity.
Iodine, 36, 85, 154, 214, 345, 354.
Iodoform, 36.
"Ionic" electrons, 380.
Ionic valency, influence of, 172.
— velocity, 169.
Ionising solvents, list of some, 137.
— — see Non-aqueous ionising solvents.
Ionium, 335.
Ions, absorption spectra of, 37.
— and electro-endosmosis, 172.
— as catalysts, 268 ff.
— colours of, 114, 390.
— gaseous, charges on, 222.
Iridium chlorides, 356.
Iron, 342.
— ammonium sulphate, 42.
— double sulphates, 351-2.
— oxides, 351.
— sol, 168.
— spectrum, 280.
— and chromium, 351.
— — magnesium, 395.
Irreversible coagulation, 175.
Isobares, 338.
Isobaric heterotopes, 338.
— isotopes, 338.
Isobutyl alcohol, 242.
Isocyanuric ester, 33.
Isothermal cell, 220.
Isotopes, 334, 354, 359, 377.

Kainite, 74-6, 78, 81.
Karlsruhe conference, 322.
Kieserite, 60, 62, 74, 75, 76, 78, 79, 81, 82.
Kinetic theory, 190 ff., 197, 201 ff., 208, 211, 271.
Krypton, 214, 333, 336, 344, 354.

Lactonitrile, 138.
Lævulinic acid, 26, 110.
— ester, 13.
Langbeinite, 78, 81, 82.
Lanthanum, 352.
— nitrate, 172.
Lattice, space, 226.
Law of Octaves, 317, 318.
Lead, 336, 337, 341.
— imide, 130.
— iodide, 134.
— isotopes, atomic volumes of, 359.
— sol, 168.
Leonite, 44, 74, 75, 76, 78, 79, 81, 82.
Liesegang's rings, 184.
Lime, 280.
Limonene, 13.
Line spectra, 274.
Lines, air, 280.
— enhanced, 282.
— long and short, 281.
Liquid crystals, 248.
Lithium, 285.
— chloride, 55.
— cupric chloride, 55.
— hydride, 358.
Litmus, 125.
Loewite, 78, 81.
Luminescence, 27, 30.
Luminophore, 30.
Lutecium, 353.
Lyophilic, 161.
Lyophobic, 161.

Macroperiodic elements, 371.
Magdala red, 168.
Magnesium, 131, 287, 288, 345, 362, 372.
— and iron, 395.
— chloride, 60, 65-75, 173.
— — hexahydrate, see Bischofite.
— oxide, 348, 351.
— potassium calcium sulphate, see Polyhalite.
— — chloride, see Carnallite.
— — sulphate, see Schönite and Leonite.
— sodium sulphate, see Astrakanite.
— sulphate, 60, 68-75, 76, 80, 81, 173. See also Kieserite.
Magnetic rotatory power, 21, 55.
— susceptibility, 20.
Magnetism and spectra, 284.
Magneto-optical anomaly, 30.
Magnets, floating, 369.
Maleic acid, 32.
Malonic acid, 27.
Mandelic acid, 260.
Mandelonitrile, 260.
Manganese, 279, 280, 333, 363.
— characteristics of, 352.
— its resemblances to other metals, 352.
— oxides, 172, 255, 352.

Digitized by Google

Mannite, 258.
Mannose, 261-2.
Mass-spectra, 336.
Mastic, 162.
— emulsions, 198, 207, 218.
Matter and electricity, 376 ff.
— — energy, 195.
— constitution of, see Atomic structure.
Mean valency, 76.
Melting-point of elements, 344-5.
Melting-points of double salts, 56.
— periodicity in, 325.
Mercuric cyanide, 86.
— iodide, 85, 134, 268.
— nitrate, 348.
— sulphate, 257, 348.
Mercury, 233, 234, 239, 342, 362.
— chlorides of, 87, 134, 348, 350.
— emulsions, 217.
— oxides of, 348.
— sols, 168.
— succinimide, 132.
— and copper, 348.
Mesaconic acid, 84.
Mesothorium-1, 337.
Mesothorium-2, 337.
Meta-elements, 331.
Metaneon, 388.
Methyl acetate, 258, 259.
— alcohol, 137, 139, 141, 146, 149, 150, 156, 267.
Methyl-glucosides, 262.
Methyl iodide, 139.
— isothiocyanate, 137.
Methyl-orange, 125.
Methyl thiocyanate, 137, 139, 141, 150.
Methyl-xylosides, 262.
Methylene blue, 168.
— iodide, 86.
Mixed crystals, 39.
Model atoms, 382 ff.
Mohr's salt, 42.
Molecular compounds, see Complex salts.
— contraction, 149.
— diameter, upper limit of, 210.
— "fragility," 271.
— instability, 392.
— magnitudes, 209 ff.
— reality, 197, 208.
— solution volumes, list of, 148.
Molecules, active and inactive, 271.
— distribution in vertical column, 201.
— "visible," 198.
— as catalysts, 269-70.
Molybdenum, 257, 343, 354.
Monomolecular reactions, 89.

N, 209 ff., see also Avogadro's constant.
N, most accurate value, 229.
— table of determinations, 229.
Naphthalene, 172, 173, 257, 266.
Nebulæ, spectra of, 386.
Nebulium, 344, 386, 387, 388.
Neodymium, 353.
Neon, 333, 334, 336, 371, 388.
Neutralisation, slow, 101, 103.
Nickel, 325.
— and copper, 349.
Niton, 333, 344, 354, 372.
Nitric acid, 268.
— oxide, 265.
Nitrides, 132.
Nitrobenzene, 80.
Nitro-copper, 350.
Nitro-ethane, 97, 103.
Nitrogen, 237, 238, 239, 256, 345, 368.
Nitrohydroquinone, 106.
"Nitro"-metallic compounds, 350.
Nitromethane, 98, 137, 139, 141, 146, 148, 150, 152, 157.
Nitro-nickel, 350.
Nitro-paraffins, 96 ff.
Nitrophenol, 105, 116, 125.
Nitrous oxide, 237, 256.
Nodal elements, 371.
Non-aqueous ionising solvents, 128 ff.
Nucleus, atomic, see Atomic nucleus.
Number, atomic, 338, 341, 353.
— gold, 181.

Oceanic salt deposits, 60 ff.
Octaves, Law of, 317.
Oenanthylic acid, 22.
Oil-drops, 223.
Oil-films, 210.
Oleic acid, 266.
Opalescence, critical, 215.
Optical activity of cobaltammines, 94.
— anomaly, 17.
— rotatory power, 25.
Order, atomic, see Atomic Order.
Orthoperiodic elements, 371.
Oscillation-frequency, 222, 283.
Oscillators, 221.
Osmium, 325.
Osmotic pressure of colloids, 164, 198.
Oxalic acid, 27, 257, 300, 308.
Oxygen, 238, 239, 254, 255, 271, 287, 343, 345.

Palladium, 350.
Paraffin oil, 242-3.
Parageneses, table of, 81.
Paragenesis, 77.
Paraldehyde, 257.
Paramagnetism, 20.
Partial valencies, theory of, 9 ff.
Partition hypothesis of colloids, 249.
Pectisation, 160.

Digitized by Google

Periodic instability, 392.
— Law, 311 ff.
— — Mendeléef's claims, 321.
— — Newlands' claims, 318.
— — apparent exceptions to, 334.
— — confirmations of, 326, 328.
— — correction of atomic weights from, 326.
— — and compounds, 329.
— — — valency, 323-4.
— surfaces, 368.
— System, 304, 305, 311 ff. See also Periodic Law and Periodic Table.
— — possible extension of, 369.
— — spiral forms of, 365.
— — transitional elements in, 332 ff.
— — and organic series, 313.
— — — spectra, 285 ff.
— Table, arrangement of, 362.
— — chief points in, 323.
— — development of, 316 ff.
— — Group I., elements in, 347.
— — — II., elements in, 348 ff.
— — — III., elements in, 351.
— — — IV., elements in, 351.
— — position of hydrogen in, 357.
— — resemblances not expressed in, 346 ff.
Permanganates, 114.
Petroleum suspensions, 170.
Phasis, 161.
Phellandrene, 13.
Phenetol, 30.
Phenol, 249-50, 258.
Phenolphthalein, 114, 115-26, 131, 132.
Phenylnitramine, 108, 110.
Phenyl-nitromethane, 99 ff.
Phosphorescence spectra, see Spectra.
Phosphoric acid, 125, 257.
Phosphorogen, 280.
Phosphorus, 363.
— oxychloride, 153-4.
— trichloride, 153-4.
Photosensitive salts, 349.
Picramide, 133.
Picric acid, 133, 242, 244, 245.
Pimelic acid, 27.
Platinum, 254, 255, 256, 258, 265, 268.
— chloride, 350.
— sols, 166, 168, 174.
Poisoning of catalysts, 265.
— — sols, 174.
Polarised light, 164.
Polyhalite, 60, 61.
Positive charges, 361.
— — in atom, 378, 381.
Positive-ray analysis, 336.
Potassamide, 132, 133.
Potassium, 285, 287, 288, 344.
— acetamide, 130.
Potassium argentocyanide, 84.
— bromide, 88, 173, 199, 228.
— calcium magnesium sulphate, see Polyhalite.
— chlorate, 40, 255.
— chloride (Sylvine), 43, 48, 63-77, 81, 178, 228, 263.
— chloroplatinate, 83.
— cuprous chloride, 44.
— cyanide, 84, 86.
— ferrocyanide, 173.
— fluoride, 228.
— iodide, 163, 228, 263.
— magnesium chloride, see Carnallite.
— — sulphate, see Leonite.
— — — — Schönite.
— nitrate, 179.
— sodium sulphate, see Gläserite.
— sulphate, 40, 42, 44, 68-75.
— tri-iodide, 36.
Periodicity in physical properties, 325.
Praseodymium, 353, 356.
Precipitation of colloids, see Coagulation.
— — — 176 ff., 250.
— — crystalloids, 247-8.
Predictions in chemistry, 326, 328, 333.
Pressure and spectra, 281.
Properties, periodicity in, 325.
Propionic acid, 242.
Propionitrile, 139, 150, 152.
Propyl alcohol, 156.
Protective action, catalytic, 258.
— — of colloids, 164, 180-1.
Protofluorine, 388.
Proto-metals, 365.
Prout's hypothesis, 312, 373.
Pseudo-acids, criteria of, 101 ff.
— colour change in, 102, 105.
— conductivity, 100, 102, 109.
— refractivity of, 110.
— salt formation by, 97 ff.
Pseudo-bases, 101.
Purple of Cassius, 162.
Pyrone, 28.
Pyruvic acid, 26.
— ester, 13.

Quanta, 222.
Quinine, 260.
Quinone, 35.
— monoxime, 101.
Quinonoid structure, 115-22.

Racemates, 43, 50, 56 ff.
Radiant energy and reactions, 270.
Radiation and Avogadro's constant, 219.
— — model atom, 381 ff.
Radioactinium, 335.

Digitized by Google

Radioactivity and Avogadro's constant, 224.
Radiothorium, 335, 337.
Radium, 335.
— and Avogadro's constant, 225, 226.
Radium-B, 341.
Radium-C_2 end-product, 335.
Radium-D, 335.
Radium-E, 342.
Rare earth elements, 280, 353 ff., 368.
— — — position in Periodic Table, 355.
Reactions addition, 10 ff.
— monomolecular, 392.
Reactivity, 13, 15.
Refractive index, 213, 215.
Refractivity, 17.
— and dissociation, 145.
— — molecular solution volume, 145.
— of pseudo-acids, 110.
— — solutions, 145.
— periodicity in, 325.
Reichardtite, 78.
Residual affinity, 7 ff.
— — conjugation of, 8.
— — rearrangement of, 9.
— — and absorption spectra, 31.
— — — boiling-point, 15.
— — — fluorescence, 27.
— — — heat of combustion, 13.
— — — luminescence, 27.
— — — magnetic rotatory power, 21.
— — — — susceptibility, 20.
— — — optical rotatory power, 25.
— — — reactivity, 8, 9, 13.
— — — refractivity, 17.
— valency, 302.
Reversible coagulation, 175, 176.
Reversion spectra, 278.
Rubidium, 273, 285, 287, 288, 344.
— racemate, 50.
— salts, 228.
Ruthenium, 325.

Salol, 172.
Salt deposits, 60 ff.
Salts, complex, 83 ff.
— double, 39-82.
Samarium, 353.
Saponin, 236.
Saturnian model atoms, 381.
Scandium, 327, 343, 354.
Scattering of α-particles, 378.
Schönite, 69-75, 76, 78, 81.
Sea-water evaporation, 61.
Sebacic acid, 27.
Selective action of solvent, 263.
Selenium, 287, 343.
Series, spectral, 283.
Shell theory of metalammines, 303.
Silica gel, 182.
Silicic acid, 159, 160, 163, 168, 169, 176, 182, 183, 247.
Silicon, 363, 372.
— and boron, 351.
— chloride, 153.
— hydride, 351.
Silk, adsorption by, 245.
Silver, 285, 323, 350.
— bichromate, 184, 185.
— chloride, 172.
— iodide, 185.
— — sol, 163.
— nitrate, 163, 184, 185, 349.
— phosphate, 349.
— sols, 166, 168, 177.
— and thallium, 349.
Slow neutralization, 101, 103.
Soap-films, 210.
Sodamide, 130, 132.
Sodium, 131, 220, 221, 277, 285, 287, 288, 343, 344.
— acetamide, 132.
— atomic volume of, 359, 360.
— bromide, 172, 228.
— chloride, 39, 43, 60, 61, 63-5, 131, 183, 228.
— fluoride, 228.
— glycocholate, 243.
— hydroxide, 163, 258.
— iodide, 228.
— magnesium sulphate, see Astrakanite.
— oleate, 236.
— potassium sulphate, see Gläserite.
— silicate, 160.
— succinimide, 130.
— sulphate, 43, 51, 78, 79, 80, 183, 236. See also Thenardite.
— sulphite, 255, 258.
— thiosulphate, 162.
Sol, 160.
Solid solution, 280.
Sols, 160.
— acquired immunity of, 178 ff.
— catalytic action of, 174.
— poisoning of, 174.
— and ferments, 174.
Solubility and dissociation, 143.
— — transition point, 48.
Solution, constant, 63.
— hypothesis of colloids, 249.
— pressure, 90.
— solid, 39, 43, 57, 280.
— volume, molecular, 145.
— volumes, list of, 148.
Solutions, 305.
— colloidal, see Colloids.
Solvates, 269.
Solvent as catalyst, 263.
— directive influence of, 263.
— power and conductivity, 142 ff.

Digitized by Google

Solvent power and di-electric constant, 150.
Solvents, mixed, conductivity in, 155.
— non-aqueous ionising, see Non-aqueous ionising solvents.
Sorption, 232.
Space-conjugation, 14, 26, 33-4.
Space lattice, 226.
Spark spectra, see Spectra.
Specific surface, 233.
Spectra, absorption, see Absorption spectra.
— arc, 280.
— band, 274, 279.
— emission, 273.
— flame, 276 ff.
— line, 274, 282 ff.
— phosphorescence, 273, 278 ff.
— reversion, 278.
— spark, 282.
— stellar, 337.
— X-ray, 275.
— and atomic numbers, 275-6, 287-8.
— — — weights, 285, 286.
— — periodic system, 285 ff.
— — pressure, 281.
— — temperature, 281, 282.
— in magnetic field, 284.
— of complex ions, 88.
— — compounds, 278.
— — elements, 273 ff.
— — nebulæ, 336.
Spectral series, 283.
Spectrometric determination of transition points, 48.
Spectrum, continuous, 274.
— of Bunsen flame, 276.
— — helium, 335.
— — hydrogen, 331-2, 335.
— Swan, 277.
Spheres, 298-9.
Spiral arrangements of the elements, 316, 365.
Stannic acid sol, 168.
— oxide gel, 182.
Stannous chloride, 162.
Starch, 159, 168, 182.
Stassfurt salts, 60 ff.
Stellar spectra, 337.
Strontium, 287, 288, 362.
Structure, atomic, see Atomic structure.
Suberic acid, 27.
Succinic acid, 27, 32, 242.
Succinimide, 130.
Sugars, 164, 261, 265, 268, 269.
Sulphur, 172, 287, 353, 354.
— chloride, 153.
— colloidal, 162.
— dioxide, 153-4, 237, 254, 257.
— trioxide, 153.
Sulphuric acid, 257.
— — constitution of, 302.
Surface action, 265.
— effects, 232.
— energy, 233.
— — and concentration, 234.
— specific, 233.
— tension, 234-6, 239.
— — "negative," 251.
— — static and dynamic, 236.
Surfaces, periodic, 368.
Suspensions, 158.
Suspensoids, 160, 246.
Swan spectrum, 277.
Sylvestrene, 13.
Sylvine, see Potassium chloride.
Symmetry and asymmetry, 260-1.

Talose, 261-2.
Tannin, 159.
Tantalum oxide, 356.
Tartaric ester, 25.
Tautomerism, double symmetrical, 29.
Telluric helix, 315.
Tellurium, 343.
Temperature and spectra, 281, 282.
Tensimeter, 46.
Terbium, 353.
— group, 368.
Terpenes' heats of combustion, 13.
Tesla discharge, 27.
Tetra-ethyl-ammonium iodide as a soluble, 135 ff.
Tetramethyl ammonium hydroxide, 393.
— ferrocyanide, 300.
Tetranitro-methane, 112.
Thallium, 273, 287, 342.
— and alkali metals, 349.
— — copper, 348.
— — gold, 349.
— — silver, 349.
— compounds, 40, 348, 349, 350.
Thenardite, 74, 75, 80, 81.
Thermometric determination of transition point, 48.
Thorium, 335, 395.
— compounds, 168, 356, 377.
— and uranous salts, 377.
Thorium-lead, 359.
Thorium-X, 335.
Thulium, 353.
Tin, 154.
Titanic acid, 168.
Titanium, 354, 363.
Transition interval, 50.
— point, determination of, 45 ff.
— temperature, 48.
Transitional elements, 332 ff.
Triethylamine, 139.
Triads, 312, 368.

Digitized by Google

Triphenylmethyl, 307.
Triple bonds, 15, 16, 24.
Tungsten, 257, 343.
Types, elementary, 335.

Ultrafiltration, 161.
Ultramicroscope, 165, 176, 189, 249.
Unsaturation and physical properties, 15 ff.
Uranium, 257, 325, 326, 343.
Uranium-2, 377.
Uranium-X_1, 377.
Uranium-lead, 359.
Uranous salts, 395.
— — and thorium, 377.

Valencies, auxiliary and main, 297.
— partial, see Partial valencies.
Valency, see also Chemical affinity and Residual affinity.
— and absorption spectra, 37.
— — atomic number, 341.
— — β-ray changes, 377.
— — coagulating power, 179.
— — colour of ions, 390.
— — Periodic Law, 328-4.
— change in catalysis, 267.
— contra-, 304.
— electronic views of, 306 ff.
— free positive and negative, 302.
— latent, 302.
— mean, 76.
— polar and non-polar, 291.
— residual, 302.
— theories of, 289 ff.
Vanadium, 363.
— oxide, 356.
Van der Waal's equation, 214.
Vanthoffite, 78, 81.
Velocity of ions and colloid particles, 169.
Violuric acid, 110.
Viscosity and conductivity, 140 ff., 143.
— — transition point, 49.
— of colloids, 160, 246.
— — gases and molecular magnitudes, 212, 214.
"Visible molecules," 198.
Volume, atomic, see Atomic volume.
— molecular solution, 145.
Vortex-atoms, 374.

Water as a catalyst, 264.

x, 334.
X-ray spectra, 275, 353, 355, 356, 360, 380.
— — and atomic order, 339, 342.
— — of isotopes, 337.
— spectrometer, 227.
Xenon, 214 333, 344, 354.

y, 334.
Ytterbium, 353.
Yttrium, 354.

Zero group, 332, 344.
Zinc, 354, 362, 372.
— compounds, 42, 49, 172, 257, 348, 351.
— potassium sulphate, 42.
— sulphide, phosphorescent, 224, 225, 279, 280.
Zirconium, 354, 363.

PRINTED IN GREAT BRITAIN BY THE UNIVERSITY PRESS, ABERDEEN

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

Digitized by Google

THIS BOOK IS DUE ON THE LAST DATE STAMPED BELOW

AN INITIAL FINE OF 25 CENTS WILL BE ASSESSED FOR FAILURE TO RETURN THIS BOOK ON THE DATE DUE. THE PENALTY WILL INCREASE TO 50 CENTS ON THE FOURTH DAY AND TO $1.00 ON THE SEVENTH DAY OVERDUE.

FEB 8 1933
OCT 8 1934

DEC 28 1943
JAN 11 1944 R
JAN 25 1944 R 2
FEB 8 1944 R3
FEB 22 1944 R4

OCT 26 1934

MAR 20 1936

FEB 17 1937

OCT 5 1942

LD 21-2m-1,'38 (52m)

Digitized by Google

YC 21602

691557

QD453
S83

UNIVERSITY OF CALIFORNIA LIBRARY

Digitized by Google